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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1907.

ISSUED BY THE CHEMICAL SOCIETY.

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PREFACE.

In order to render the Annual Reports as comprehensive as possible, slight variations will be made in the list of sections from time to time. For example, the Reports for 1908, while embracing as heretofore sections on Agricultural, Analytical, Inorganic, Organic, Physiological, General and Physical Chemistry, will include a Report on Crystallography in the place of Mineralogy, and advances in Stereochemistry will be embodied in the sections directly concerned instead of being placed in a separate division. The Report on Radioactivity, postponed until 1909, will cover the interval since the present issue.

J. C. C.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
Abstr.	Abstracts in Journal of the Chemical Society.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. of Botany.	Annals of Botany.
Ann. Report.	Annual Reports of the Chemical Society.
Anzeiger K. Akad. Wiss. Wien.	Anzeiger der Kaiserliche Akademie der Wissenschaften in Wien.
Apoth. Zeit.	Apotheker Zeitung.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Brit. Med. J.	British Medical Journal.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Trade J.	Chemical Trade Journal.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Gazzetta	Gazzetta chimica italiana.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Landw.	Journal für Landwirtschaft.
J. pr. Chem.	Journal für praktische Chemie.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.

ABBREVIATED TITLE.	JOURNAL.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc.	Proceedings of the Chemical Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Trans.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Wien. Sitzungsber.	Sitzungsberichte der Kaiserliche Akademie der Wissenschaften in Wien.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

ERRATA.

Page.	Line.	
49	4*, 5*	in formulæ *for* "Br" *read* "B_2."
51	15	*for* "precipitated" *read* "precipitant."
54	12	,, "condensed" *read* "volatile."
56	23	*add* "(Whitehouse, *Abstr.*, 1907, ii, 680)."
58	8	*for* "from" *read* "about."
74	4*	,, "hydrogen" *read* "nitrogen."
79	11*	,, "identified" *read* "indicated."
79		In reference No. 31 to Fenton and Sisson, *for* "376" *read* "385."
81	8	*for* "$-CH_3-$" *read* "$-CH_2-$."
87	1*	,, "$3C_6H_{12}O_6{\cdot}2N_3H_5$" *read* "$3C_6H_{12}O_6,2CN_3H_5$."
93	10*	,, (the second) "$\longrightarrow$" *read* "+."
94	14	,, "H_2O" *read* "$2H_2O$."
98	7	,, "disulphates" *read* ' disulphate."
101	2	,, "R. Scholl (1896)" *read* "Scholvien (1885)."
103	10*	Insert reference to Wohl and Schweitzer, namely, *Abstr.*, 1907, i, 194.
105	1	*for* "the way" *read* "this way."
211	1*	,, "Graeffe" *read* "Graefe."
223	11	,, "Schworzoff" *read* "Sckworzoff."

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* From bottom.

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GENERAL AND PHYSICAL CHEMISTRY.

In the following Report, no attempt has been made even to refer to all the numerous researches which have been published during the past year. Not a few of these have been occupied chiefly with the application of physico-chemical principles and methods to the elucidation of special problems in inorganic or organic chemistry, and their results are therefore more appropriately referred to in the sections of the Report dealing with these branches of the subject. It has, however, been the endeavour of the writer to call attention to the more prominent and generally interesting investigations of the preceding year in such a way as to give a fair view of the lines of advance and progress made in this branch of chemistry.

Valency and Volume.

During recent years, the doctrine of valency has received not a little attention, the result of which is to assign to valency more and more the character of a volume function. This conclusion is in so far noteworthy that it has been reached by different investigators from an examination of different experimental data; but whether, as I. Traube supposes, volume is causally related to valency, or whether valency and volume are related expressions of some more fundamental property, cannot yet be said to have been established.

The interesting theory connecting valency and volume which was put forward a year ago by W. Barlow and W. J. Pope,[1] has received fuller consideration, and the crystallographic relations of a number of inorganic substances have been studied.[2] It is pointed out that there are two, and only two, ways (which, however, may also be homogeneously combined) in which equal spheres can be most closely packed so as to form a homogeneous structure, namely, the cubic and the hexagonal. In the case of the latter, the axial ratio $a:c$ will have the value 1 : 1·6330 or 1 : 1·4142. On examining the crystalline form of the elements, it is found that about 85 per cent. crystallise, as a matter of fact, in either the cubic or the hexagonal system. In the case of the elements which deviate from this behaviour, the crystalline form can be easily explained by the assumption that the constituent spheres possess a slight polarity, or that some of the spheres differ slightly in size from the others. The elements copper, silver, gold, carbon, silicon, lead, arsenic, vanadium, iron, platinum, iridium, osmium, palladium, titanium, thorium, germanium, mercury, gallium, chromium, and nickel crystallise in the cubic system, and their crystal structures are therefore appropriately represented by the cubic most closely packed assemblage of equal spheres. The elements magnesium, zinc, cadmium, glucinum, carbon, arsenic, antimony, bismuth, and tellurium crystallise in the hexagonal system, or in one of its sub-divisions, and exhibit axial ratios lying between 1 : 1·3035 and 1 : 1·6242, approximating therefore to those of the most closely packed hexagonal assemblage of equal spheres, namely, 1 : 1·6330 or 1 : 1·4142. The deviations found can be explained by assuming a slight expansion of some of the constituent spheres of the most closely packed assemblage.

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[1] *Ann. Report*, 1906, 1.

[2] *Trans.*, 1907, **91**, 1150.

In the case, also, of binary compounds, since these are for the most part composed of two elements of the same valency, and are, accordingly, built up of spheres having approximately the same volume, it follows that these compounds will, for the most part, crystallise in forms of the cubic or hexagonal system, and, indeed, it is found that about 88 per cent. of such compounds do have such crystalline forms. In the case of binary cubic compounds, however, it is found that they only rarely exhibit holohedral symmetry. The particular hemihedry or tetartohedry exhibited is, however, capable of explanation on the basis of the theory, and the authors are also able to give an explanation of polymorphism and other crystalline properties of substances.

The fundamental assumptions made by Barlow and Pope lead to the conclusion that the atomic spheres of influence are directly proportional in volume to their fundamental valencies. It might therefore be expected that this relationship between valency and volume would be traceable throughout a series of homologous compounds, and this has been found by G. Le Bas[3] to be true, at least, in the case of a number of higher hydrocarbons. When the molecu-

[3] *Trans.*, 1907, **91**, 112; *Abstr.*, 1907, ii, 754.

lar volumes of different compounds, as determined by Krafft at the temperature of the melting points, are compared, it is found that the quotient of the molecular volume by the number of valencies in the compound has a mean value of 2·970. This, then, is the unit valency volume or valency stere (the atomic volume of hydrogen in combination). Further, the mean difference in the molecular volumes of two adjacent members of the series is 17·83, which represents therefore the molecular volume of the group CH_2. Since the number of valencies in this group is six, then, on the assumption that the volume is proportional to the valency, the molecular volume should be $6 \times 2·970 = 17·82$, which is in complete harmony with the experimental value. It will thus be seen that the molecular volumes of the hydrocarbons are additively equal to the sum of the atomic volumes of hydrogen and carbon when the atomic volume of hydrogen is taken equal to 2·970 and that of carbon to 11·88 (volumes taken proportional to the valencies). These values, the author shows, are in better agreement with experiment than those given by Kopp or by Schröder.

With regard to the higher normal paraffins in the liquid state, it is further shown that the above relations hold, not only at the melting points, but also at *equal intervals* of temperature above them. It is thus evident that the temperature conditions under which the greatest regularity with respect to the volume relations of compounds is obtained, do not coincide with the corresponding states according to the theory of van der Waals. An examination of the volumes of the simpler hydrocarbons shows that the additive valency relation given above holds more nearly when determined at corresponding reduced pressures than at corresponding reduced temperatures, and, under the former condition, there is less divergence at considerable intervals from the critical state than at the critical point itself.

The connexion between refractivities and valency is also mentioned by Le Bas, but this question has been much more fully studied by I. Traube.[4] Traube distinguishes three different volumes: (1) The molecular co-volume, or the space filled with free ether. It is the quantity $(v-b)$ of the van der Waals' equation. (2) The outer volume of the atom, or the volume which the atom occupies in the molecule *plus* the envelope of bound ether. It is the quantity b of the van der Waals' equation. (3) The inner volume of the atom (nuclear volume), or the volume occupied by the actual mass of the atom as such. (4) The atomic co-volume, which is the difference between the outer volume and the inner volume. It is the space occupied by the electrons. Now, it has been shown previously by Traube, that the factor b of the van der Waals' equation is approximately equal to four times the atomic refractivity (according to the Lorenz-Lorentz formula), and, since b is also approximately equal to four times the inner volume of the atom, it follows that the refractivity can be taken as an approximate measure of the latter.

---

[4] *Abstr.*, 1907, ii, 145, 205, 207.

Traube has collected the values of the molecular refractivity of a considerable number of organic substances containing carbon, nitrogen, oxygen, and hydrogen, and finds that the atomic refractivities for the red hydrogen line are in the ratios 4 : 3 : 2 : 1; that is to say, in the ratio of the valencies of the atoms, oxygen appearing as bivalent. The value of the refractivity unit (refractivity stere) for each valency is, on an average, 0·787 (deviations of ±1 per cent.). From this, it follows that compounds having the same valency number will also have the same molecular refractivity (for example, C_3H_8O and $C_3H_6O_2$; valency number = 22; molecular refractivity 17·42). From the above, it follows that the inner volume is proportional to the valency.

Further, if one identifies valency with the activity of electrons or of groups of electrons (to which the author gives the name valon), then it follows from the preceding generalisation that the inner volumes of atoms stand in simple multiple relations, their values being proportional to the number of valons surrounding the atom. It also follows that the valency number of a compound, and hence the valency of the constituent atoms, can be obtained by dividing the molecular refractivity by the value of the stere, 0·787. On carrying out the calculation, it is found that the inner volumes (which, according to the above, are proportional to the valencies) of fluorine, chlorine, bromine, iodine, sulphur, selenium, zinc, mercury, tin, and lead in organic compounds are 1, 7, 11, 17, 10, 14, 16, 18, 22. That is to say, whereas the molecular refractivity of fluorine compounds can be calculated on the assumption that fluorine is univalent, it is necessary to suppose chlorine to have a valency of 7, bromine of 11, and so on. From this, the author concludes, not that chlorine has six subsidiary valencies, but that individualised valons (or electrons) do not exist associated with the atom, and that there is only a valon space uniformly filled with ether. The septavalency of chlorine therefore is due, not to its being surrounded by seven valons, but to its valon volume being equal to seven times the value of the stere. From a consideration of the volume relations at the absolute zero, at the critical point, and at the boiling point, it is shown that the valency volumes correspond with the above numbers.

The above relationships do not hold for associated liquids. These are considered by Traube, not as atomic compounds, but as compounds existing under a greater internal pressure than the normal.

A different view of valency (not necessarily incompatible with the preceding) has been put forward by Ensrud,[5] who regards an atom as consisting of a nucleus of great, and an envelope of small, density. Between the nuclei and their envelopes, and also between the nuclei of different atoms, attractive forces exist, whereas forces of repulsion exist between the envelopes. As a consequence of this, the nucleus occupies an eccentric position. The smallest distance between the nuclei of two atoms is the valency direction or the direction of maximum force. An atom, however, may also have more than one nucleus, and so may have several valency directions, that is, the atom may be multivalent, the maximum valency being equal to the number of nuclei within the envelope. On the basis of this theory, the author is able to calculate the distance between the atoms and the atomic energy, and from the latter, the value of the ratio of the specific heat and the specific heat at constant pressure. The values calculated for the last two factors agree very well with the experimental values.

Spectroscopy.

A considerable amount of attention still continues to be devoted to the study of the ultraviolet absorption spectra for the purpose of elucidating the constitution of organic and also of inorganic substances. A new department of investigation has also been opened up by A. W. Stewart,[6] in his study of the relation between absorption spectra and optical rotatory power. On comparing the molecular rotations of the amyl esters of β-phenylpropionic acid, cinnamic acid, and phenylpropiolic acid with the absorption spectra of the free acids (the alcohol radicle being the same in each case, the change in rotation must be ascribed to the acidic part of the molecule), it was found that, although no connexion appears to exist between the absorption bands and the molecular rotation, there is a relationship between the general absorptive power and the molecular rotation in such a sense that the greater the rotation the greater is the general absorption. This rule, however, does not possess universal validity, but is applicable to substances possessing the same number of carbon atoms, and also, apparently, to members of an homologous series, as shown in the case of the absorption of formic, acetic, propionic, and butyric acids when compared with the molecular rotations of the corresponding amyl esters. The parallelism between general absorptive power and rotation is also shown in those cases where a single bond is converted into a double bond, or into a triple bond (by loss of hydrogen). The same general rule also finds application in the case of stereoisomeric substances, such as maleic and fumaric acids; not, however, in the case of structural isomerides. In the case of the former class, the more symmetrical the molecule the greater is the absorptive power.

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[5] *Abstr.*, 1907, ii, 249.

[6] *Trans.*, 1907, **91**, 199, 1537.

With regard, also, to the relationship between the absorptive power of the different isomerides of an optically active substance, Stewart has shown that, whereas the absorptive power of the two active tartaric acids is the same, mesotartaric acid has a greater general absorptive power. When concentrated solutions of the racemic acid are examined, they are also found to possess greater absorptive power than the active forms, but, as dilution proceeds, this difference in absorptive power disappears. Since such a difference is not found when two stereoisomerides, such as maleic and fumaric acids, are mixed, the author concludes that in concentrated solutions racemic molecules exist, in harmony with the work of Byk. This is borne out by the fact that solutions of astracanite above and below the transition point, 22°, exhibit different absorptive powers, so that the absorptive power may be employed for the investigation also of transition points.

With regard to the absorption spectrum of a substance in solution, it has been found to be dependent, not only on the substance, but also on the solvent, and E. von Kazay[7] has shown that the absorption bands shift towards the *red* end of the spectrum with increase in the refractive index of the liquid. This is well shown by solutions of magenta, potassium permanganate, alkannin, and chlorophyll.

Solvent.	Refractive index for the D line.	Wave-lengths.			
		Magenta.	$KMnO_4$.	Alkannin.	Chlorophyll.
Water	1·3336	552·7	570·30	—	—
Ether	1·3566	—	—	564·51	612·8
Alcohol	1·3654	559·68	579·2	—	—
Chloroform	1·4490	—	—	572·86	618·0
Glycerol	—	567·83	—	—	—
Carbon disulphide	1·6308	—	—	579·20	—

Moreover, since the refractive indices give the relative velocities of light in the liquids, the shifting of the bands can be calculated by means of the Doppler principle $\lambda_1=\lambda(1\pm c/v)$, where λ_1 is the wave-length of the shifted line, λ the wave-length of the original line, c the difference of the compared velocities, and v the velocity of propagation of light in air.

[7] *Abstr.*, 1907, ii, 919.

Refractivity.

Although in many cases the refractive index of a substance can be calculated from the refractive power of its solutions, other cases, not few in number, have also been met with where the refractive index so obtained, not only differs from that obtained with the solid substance, but depends also on the solvent. At first this behaviour was considered to be due to ionisation, but it was found later that many cases could not be explained on this view. Recently, the subject has again been studied by Walden,[8] in pursuance of his previous work on non-aqueous solutions. This author has determined the refractive indices of tetraethylammonium iodide, tetrapropylammonium iodide, and phenyldimethylethylammonium iodide in a large number of different solvents. Whilst the refractive index of these substances, calculated by the mixture formula, has been found to vary only slightly with the concentration of the solution, the values calculated from solutions in different solvents have been found to differ very considerably from one another. These differences cannot be ascribed to variation in the degree of ionisation, because it has been found that they occur even in solutions in which the degree of ionisation is the same, and, further, in solutions in which the degree of ionisation is different, the same value for the refractivity has been obtained. In considering other physical properties of the solute and solvent, however, the author shows that the molecular volume of a substance in solution is a variable quantity according to the solvent employed. Thus for tetraethylammonium iodide in aqueous solution, the molecular volume is 186·9, whereas in acetonitrile solution it is only 157·1. The molecular volume, however, varies only slightly with the concentration in any given solvent. On comparing the values of the molecular refractivity with those of the molecular volume in different solvents, it is found that the greatest value of the refractivity is found in that solvent in which the molecular volume of the solute is least, and vice versa. Moreover, it is found that the solute has the highest value of molecular volume in that solvent which has the smallest co-volume. It would therefore appear that variations in the refractivity of a dissolved substance are due to variations in its molecular volume in different solvents, and not to variations in its degree of ionisation.

With regard to the property of magnetic double refraction, it has recently been shown by Cotton and Mouton[9] that this property is exhibited by all liquids belonging to the aromatic group, so far as these have been studied. This is the first occasion on which this property has been observed in the case of pure liquids. The property is not possessed, apparently, by liquids belonging to the fatty series. Carbon disulphide exhibits a small, but negative, double refraction.

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[8] *Abstr.*, 1907, ii, 519.

[9] *Ibid.*, 727.

Photo-chemical Reactions.

During the preceding years, the study of the mechanism of reactions taking place under the influence of light has attracted more and more attention. In the case of gas reactions, more especially, the retarding or accelerating influence of impurities on the reactions has aroused considerable interest and debate. The subject has, during the past year, been again taken up by D. L. Chapman, Chadwick, and Ramsbottom,[10] who have studied, more especially, the effect of moisture on the combination of carbon monoxide with oxygen under the influence of ultraviolet light obtained from a mercury lamp. As a result of these experiments, it has been found that, on exposure of a mixture of carbon monoxide and oxygen to the action of ultraviolet light, there is formation both of ozone and of carbon dioxide, and the ratio of carbon dioxide to ozone is nearly the same no matter whether the gas mixture has been well dried over phosphoric oxide or only imperfectly dried by means of sulphuric acid. If, however, the gas mixture is saturated with moisture, the amount of carbon dioxide as compared with the ozone is very greatly increased. Thus, with the dried gases, the ratio of carbon dioxide to ozone was about 1 : 2, whereas in the case of the gases saturated with moisture the ratio was about 20 : 1. The change in the composition of the final gas mixture, which is caused by the presence of water, leads the authors to the view that the water alters the distribution of the vibrational energy in the system, the state of vibration of the carbon monoxide and the oxygen molecules being altered so as to lead to increased combination. This view receives some confirmation from the fact that, when dry carbon dioxide is exposed to the action of ultraviolet light, a certain amount of decomposition takes place which is increased by reduction of pressure. In the case of the moist gas, however, practically no decomposition occurs.

Phosphorescence and Fluorescence.

The view has been expressed by J. J. Thomson that a corpuscular group, forming part of an atom, gives rise to light when its internal energy exceeds a certain minimum value, the critical energy, and this value may be attained either by elevation of temperature or by the introduction into the corpuscular system of new corpuscles. On the basis of this idea, J. de Kowalski[11] proposes a new theory of phosphorescence and fluorescence. He assumes that every phosphorescent substance is composed of two distinct kinds of corpuscular systems, which he calls electrogenic and luminophoric systems. An electrogenic system has the property of expelling electrons under the action of external energy, for example, light. This constitutes the secondary radiation given out by bodies, and, from the fact that these secondary radiations vary in different systems, it is to be concluded that different systems are not electrogenic to the same extent. A luminophoric system, on the other hand, is one the internal energy of which is very near to the critical energy. In order to become luminous, therefore, it is sufficient for it to absorb a relatively small number of electrons. Each atom may contain one or several luminophoric groups, but each luminophore can give rise to only one kind of light possessing a definite spectrum.

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[10] *Trans.*, 1907, **91**, 942.

[11] *Compt. rend.*, 1907, **144**, 266.

On these assumptions, the mechanism of phosphorescence and fluorescence can be explained as follows. Light causes the expulsion in large numbers of electrons from systems which are strongly electrogenic. As these are intimately connected with the luminophores, the secondary rays can penetrate into the latter, provided their velocity is appropriate; the critical internal energy of the luminophore is soon exceeded, and light is produced. This luminosity will continue until, by the expulsion of electrons, the energy has been reduced to a value below the critical value. In the case of fluorescence, the electrons are not permanently absorbed, but during their passage through the luminophore they make the latter luminous.

The author finds confirmation of his assumption of the two kinds of corpuscular groups in the known facts of phosphorescence. The experiments of others have shown that phosphorescence occurs only when there are two different substances in contact, the active metal and the diluent. It is the former of these that plays the part of luminophore. The author has also obtained a quantitative relationship between the intensity of phosphorescence and the time, which has the form $I = Ae^{-\alpha t} - B$, where A, α, and B are constants depending on the temperature.

The experimental study of the phosphorescence of mixtures of the rare earths or of manganese with the alkaline earths has been made by J. de Kowalski and Garnier,[12] and by Bruninghaus.[13] An optimum of phosphorescence occurs when the mixtures are made in certain proportions.

The phosphorescence of uranium salts and of other substances at the ordinary temperature and at the temperature of liquid air has been studied by H. Becquerel.[14] In the case of the uranium

[12] *Abstr.*, 1907, ii, 418.

[13] *Ibid.*, 419.

[14] *Ibid.*, 322; see also *ibid.*, 213.

salts, but not in the case of the other substances examined, the brightest portions of the spectrum are displaced towards the red end, but it is not yet certain whether this displacement is the result of new luminous movements or is due to the brightening of bands existing feebly in the spectrum emitted at the ordinary temperature.

With regard to the fluorescence of organic compounds, J. Stark[15] points out that fluorescence is always determined by absorption in a band spectrum, and the absorption spectrum (in the ultraviolet) of all fluorescing substances is a banded spectrum. When carbon in the benzene ring is replaced by oxygen, sulphur, or nitrogen, analogous changes are also produced in the position and intensity of the bands of the absorption and fluorescence spectrum. It follows from this therefore that the same connexion must exist between chemical constitution and fluorescence as between chemical constitution and absorption. Since it is a well-known fact that all aromatic compounds possess a banded absorption spectrum, one would also expect all aromatic compounds to be fluorescent. This the author finds to be the case.[16] By the introduction of different groups, the position of the fluorescence spectrum may be altered, and thus may appear in the visible region. The above work is in harmony with that carried out by Francesconi and Bargellini,[17] who also found that all aromatic compounds are actually or potentially fluorescent (in the visible region), but that aliphatic compounds are non-fluorescent.

A considerable amount of discussion has taken place during the past year between Hantzsch and Kauffmann[18] on the question of the relationship between chemical constitution and colour. When a colourless substance, on being converted into a salt, becomes coloured, it is assumed by Hantzsch that a distinct change in chemical constitution has occurred, whilst, on the auxochrome theory of Kauffmann, it is due to a shifting of the absorption bands under the influence of a new group.[19]

Kauffmann has also further extended his views with regard to colour and constitution.[20] Two kinds of chromophoric groups are to be distinguished, namely, dependent chromophores and independent chromophores. The former give rise to colour only by combination with the partial valencies of the luminophore groups, whereas independent chromophores give rise to colour without requiring the presence of partial valencies. Independent chromophores readily cause colour in the aliphatic series, whereas dependent chromophores can do so only when in combination with other unsaturated groups.

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[15] *Abstr.*, 1907, ii, 147.

[16] *Ibid.*, 418.

[17] *Ann. Report*, 1906, 27.

[18] *Abstr.*, 1907, i, 127, 513; ii, 519.

[19] See also Hewitt and Mitchell, *Trans.*, 1907, **91**, 1251.

[20] *Abstr.*, 1907, ii, 519.

Volume of Substances in Solution.

Assuming the change in volume which occurs on solution to depend only on the solute, Lumsden[21] has calculated the molecular solution volume at different temperatures of various solutes for a number of cases in which it could reasonably be assumed that chemical reaction between solvent and solute does not occur. In the first place, it was found that the molecular volumes so calculated did not show any sudden change on passing through the melting point or boiling point of the solute, so that it may be inferred that whatever relation exists between the molecular solution volume and the molecular volume of a liquid (above its melting point) will also hold for the volume of a supercooled liquid. In the cases examined, in which only organic solvents were employed, it was found that the molecular solution volume, calculated in the above manner, either coincided with the molecular volume of the pure liquid solute, or, if not, then the molecular volumes in the pure state and in solution differed by the same amount at different temperatures. In other words, the curve of molecular volumes of the pure solute at different temperatures coincides with, or is parallel to, the curve of molecular solution volumes. Consequently, the volume occupied by a substance in solution is the same as that of the pure substance at the same temperature in the liquid state, or, if it is not identical, it deviates by the same amount at all temperatures. The volume of a substance in solution, however, depends, not only on the solute, but also on the solvent, and to a certain extent also on the concentration, and this the author attributes to differences in the molecular interspaces of the solvent, or the co-volume of the solvent, a conclusion in harmony with the work of Walden on the refractivity of substances dissolved in different solvents (p. 7).

Osmotic Pressure.

The subject of osmotic pressure is one which still continues to attract the attention of a number of workers, not only on the experimental, but also on the theoretical and speculative, sides. On the experimental side, Morse and Frazer, assisted by various co-workers, have extended the measurements referred to in the last Report[22] by measurements of the osmotic pressure of solutions of dextrose and of sucrose at temperatures in the neighbourhood of 0° and 5°.

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[21] *Trans.*, 1907, **91**, 24.

[22] *Ann. Report*, 1906, 9.

As in the case of sucrose,[23] Morse, Frazer, and Lovelace[24] have found that in the case of dextrose, also, aqueous solutions at temperatures in the vicinity of 20° exert an osmotic pressure equal to that which a molecular equivalent quantity of a gas would exert if its volume were reduced, at the same temperature, to that of the *solvent* in the pure state. The following are the figures obtained (at temperatures between 22° and 26°):

Weight normal concentration (mols. in 1000 gms. of solvent.)	Observed osmotic pressure.	Theoretical gas pressure at the same temperature.	Mean mol. weight for each concentration.
0·1	2·39 2·42	2·42 2·43	180·62
0·2	4·76 4·77	4·85 4·86	181·94
0·3	7·12 7·17	7·22 7·25	181·06
0·4	9·70 9·65	9·78 9·77	180·62
0·5	12·07 12·00	12·03 12·12	179·35
0·6	14·56 14·32 14·29	14·46 14·40 14·45	179·62
0·7	16·82 16·96 16·75	16·85 17·04 16·88	179·63
0·8	19·27 19·16 19·25	19·31 19·33 19·35	179·76
0·9	21·64 21·49 21·63	21·80 21·70 21·74	179·99
1·0	24·12 24·00 24·03	24·08 24·11 24·07	179·04
			180·08

Mean calculated mol. weight = 178·74.

On determining the freezing points of the solutions, it was found that the depression of the freezing point is proportional to the weight of dextrose dissolved in a fixed quantity of water. The molecular depression was found, however, to be 1·92°, instead of the theoretical 1·85°.

Morse and Frazer, assisted by Holland, Dunbar, and Rogers,[25] have also measured the osmotic pressures of sucrose solutions at about 0° and 5°, and of dextrose solutions at about 0°, and in all three cases values for the osmotic pressure have been obtained which are considerably higher than the theoretical gas pressure, *the values, indeed, being practically the same as those obtained at* 20°. As to the explanation of this unforeseen result, little can be said at present, the experimental data being still too scanty. The authors, however, point out that the deviations of the observed from the calculated osmotic pressures at 0° are in the same direction as the deviations of the observed molecular depressions of the freezing point from the theoretical value 1·85°. Indeed, in the case of dextrose, the ratio of observed pressure to theoretical pressure is practically the same as the ratio of observed molecular depression to the theoretical depression. It may be recalled that the authors have stated [26] that the depression of the freezing point in the case of solutions of sucrose is proportional, not only to the weight normality, but also to the density. In the case of solutions of dextrose, the depression is proportional to the weight normality only. Further work is necessary, however, in order to elucidate the effect of temperature on the osmotic pressure, and it is very desirable that measurements of the vapour pressure of the solutions at various temperatures should also be carried out.

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[23] *Ann. Report*, 1906, 10.

[24] *Abstr.*, 1907, ii, 439.

[25] *Ibid.*, 440, 533, 744.

With regard to work of a theoretical and speculative character in connexion with osmotic pressure, attention must be called, in the first place, to the alleged connexion between osmotic pressure and surface tension. Some years ago, Battelli and Stefanini [27] stated that they had found that, not only a qualitative, but also a quantitative relationship exists between the value of the osmotic pressure and the surface tension of solutions in such a way that solutions having the same surface tension have also the same osmotic pressure, and hence, also, the same freezing point and vapour pressure; and they saw in the tendency to equalise the surface tension, the driving force which gives rise to osmotic pressure. During the past year, the same authors sought to establish their views, not only by further experimental work, but also by a mathematical deduction of the supposed relationship.[28] On account of the fact that other workers have found in the views of Battelli and Stefanini support for other speculations, the writer considers it necessary to emphasise the fact that neither experiment nor mathematics supports the views of the Italian investigators. The mathematical deduction was on the following lines. Two capillary tubes are placed, one in the solvent and the other in the solution, and the upper ends of the tubes are connected by a space filled with the vapour of the solvent. The authors then assume that there is a condition of equilibrium when the liquid in the two tubes has risen to a certain height depending on the surface tension of the liquids, and deduce therefrom a relation between capillary rise and vapour pressure, and hence, also, osmotic pressure. This deduction is, however, invalid on account of the fact that the primary assumption is contrary to fact. Under the conditions supposed by the authors, no equilibrium exists, but, rather, distillation would take place from the tube containing the pure solvent to that containing the solution, and this distillation would continue until the solution had the same composition as the pure solvent, that is, equilibrium would never be attained.[29] Known experimental data also show the falsity of the authors' views. Solutions of, say, salt and of salicin can be prepared which have the same osmotic pressure, but, whereas salt solutions have a surface tension greater than that of water, solutions of salicin have a surface tension less than that of water. It is therefore impossible for salt solutions and salicin solutions to have, at the same time, equal osmotic pressure and equal surface tension. The existence of the supposed connexion between osmotic pressure and surface tension can therefore no longer be sustained. The basis on which these views were developed, namely, the connexion stated by I. Traube to exist between surface tension and *direction of flow* of liquid through a membrane (imperfectly semipermeable), may, however, still retain its interest, especially in biological work, but it has no importance for the fundamental problem of solutions.

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[26] *Ann. Report*, 1906, 10. [27] *Ibid.*, 1905, 5. [28] *Abstr.*, 1907, ii, 233.

In connexion with the experimental work at present being carried out on the direct measurement of osmotic pressures of considerable magnitude, a mathematical paper published by A. W. Porter[30] deserves attention. This author here takes account of the effect of hydrostatic pressure on the value of osmotic pressure, and has obtained an equation connecting osmotic pressure and vapour pressure of a solution for any given concentration, of any degree of compressibility, and under any hydrostatic pressure. If the osmotic pressure is defined under such conditions that the *solvent* is under the hydrostatic pressure of its own vapour, the formula reduces to that of van't Hoff, provided the assumption is introduced that the solution is incompressible, and that the vapour follows the gas laws, but, if the conditions are such that the *solution* is under the hydrostatic pressure of its own vapour, the equation reduces to that put forward by the Earl of Berkeley.[31] From the difference of compressibility of solvent and solution, it follows that the osmotic pressure and also the vapour pressure will differ according as solvent or solution is under hydrostatic pressure. The author therefore recommends that the values of osmotic pressure and vapour pressure should always be reduced to that corresponding with a solution under the pressure of its own vapour alone.

On account of the fact that in very dilute solutions laws obtain which are analogous to the ordinary gas laws, the assumption has from time to time been made that the deviations which are found in the case of rather more concentrated solutions are of the nature of the deviations of gases from the simple laws. It has therefore been sought to obtain for solutions an equation similar to that of van der Waals for gases. During the past year, the Earl of Berkeley[32] has found that the following formulæ represent the experimental data with fair success: (1) $(A/v-p+a/v^2)(v-b)=RT$. (2) $(A/v+p-a/v^2)(v-b)=RT$. In equation (1), v is the volume of the *solvent*, which contains 1 gram-molecule of solute, and in (2), v is the volume of *solution*, which contains 1 gram-molecule of solute. The following table shows the degree of agreement for solutions of sucrose:

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[29] Compare A. Sella, *Abstr.*, 1907, ii, 934.

[30] *Abstr.*, 1907, ii, 743.

[31] *Ann. Report*, 1906, 11.

Conc. in gms. per litre of solution.	Calculated osmotic pressure.		Observed osmotic pressure.
	for $v_{(1)}$.	for $v_{(2)}$.	
850	(183·0)	(183·0)	(183·0)
760	(133·7)	(133·7)	(133·7)
660	(100·8)	(100·8)	(100·8)
540	68·4	67·7	67·5
420	45·0	43·4	44·0
300	27·7	25·4	26·8
180	14·6	12·2	14·0

In an addendum to the paper, it is pointed out by Professor Larmor that the free energy of a solution at constant temperature can depend only on the ratio of the *masses* of solute and solvent present. In the case of aqueous solutions, therefore, it is a function of the ratio of the mass of the solute to the volume of water. The latter is $(v-b)$, where v is the volume of the solution, and b may be taken as a constant. According to Willard Gibbs, the function (applicable to very dilute solutions) must be of the form $-C\log(v-b)$. The variation of the available energy must be equal to $-pdv$, and hence $p=C/(v-b)$. At extreme dilution, b is negligible compared with v, and the usual argument shows $C=RT$. On this reasoning, therefore, the second of the above equations should be preferable for dilute solutions, or solutions of only moderate concentration. There still remains the question, however, whether, in this case, RT actually corresponds to the universal gas constant; it must do so on the gas theory, but the application of the doctrine of available energy to osmotics leaves room for slight discrepancy caused by the attraction of the solvent and solute molecules, such as is represented by the term A/v.[33]

During the past year, a modified kinetic theory of osmosis was put forward by Lowry.[34] According to this theory, the diminution of

[32] *Abstr.*, 1907, ii, 440.

[33] See also Bogdan, *ibid.*, 153.

[34] *Trans. Faraday Soc.*, 1907, **3**, 14.

vapour pressure by the solution of a substance in a liquid is due to a blocking action of the solute molecules at the surface of the solution, which retard the escape of the water molecules from within the solution, but are considered not to have any influence on the condensation of vapour. On this view, there ought to be some connexion between the osmotic pressure and the surface structure, and therefore surface tension, of the solution, and the theory of Battelli and Stefanini (*supra*) is cited in favour of this. As the author points out, the theory holds only for dilute solutions. The difficulties therefore which have prevented physical chemists from giving acceptance to the kinetic theory as a quantitative theory of solutions still remain.[35]

Since, in recent years, much discussion has taken place round the deviations of concentrated solutions from the simple gas laws, the writer would take this opportunity of emphasising the necessity for workers on osmotic pressure of testing the results of their measurements, not by the simplified equations which are commonly used in the case of dilute solutions, but by the more exact thermodynamic formulæ as applied to concentrated solutions, for example, the formulæ deduced by van Laar by application of the thermodynamic potential. According to this, the deviations of concentrated solutions from the dilute solution laws are not only not the same in magnitude as the deviations of gases from the gas laws, but are in different directions. In the light of this, also, the attempts to apply the van der Waals' equation to solutions should be viewed.

Aqueous Solutions.

The study of aqueous solutions still continues to engage the attention of a number of workers, and during the past year the results of a considerable number of experiments, carried out along various lines, have been published. In some cases these have been, not only adduced in support of the view that hydrates are formed in solution, but they have also, in some cases, been employed for the calculation of the extent to which hydration occurs. Thus H. C. Jones and Uhler[36] have investigated the absorption spectra of aqueous solutions of copper and cobalt chlorides and copper bromide, and the effect of the addition to these solutions of calcium chloride, calcium bromide, and aluminium chloride. As the result of these experiments, it was found that addition of the last-mentioned substances had the same effect on the absorption as concentration of the pure solution of copper or cobalt salt, and the effect is greatest in the case of aluminium chloride. This is therefore regarded as evidence that the calcium and aluminium chlorides combine with a certain amount of the solvent water (they become hydrated) and consequently there is less water available for the coloured salts. The same authors have also investigated the change in the absorption spectra on the addition of water to solutions of copper chloride in methyl alcohol, ethyl alcohol, and acetone, and of cobalt chloride in methyl alcohol. In these cases, also, addition of water to the anhydrous solvents causes a change in the absorption spectra similar to that produced by dilution of the aqueous solutions. These experiments are also adduced in support of the view that the coloured salts are hydrated in solution, the amount of hydration increasing with the dilution.

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[35] See also "General Discussion on Osmotic Pressure," *Trans. Faraday Soc.* 1907, **3**, 12.

[36] *Abstr.*, 1907, ii, 147, 211, 212.

Whereas the experiments just quoted are only of a qualitative nature, the results of other experiments have been communicated which, on the basis of certain assumptions, enable the degree of hydration of the solute to be calculated. The methods employed have been various. In the first place, H. E. Armstrong, assisted by several co-workers (J. V. Eyre, A. V. Hussey, W. P. Paddison, R. Whymper, J. A. Watson, and R. J. Caldwell), has investigated (*a*) the diminution of the solubility of sodium chloride, potassium chloride, and ammonium chloride on addition of varying amounts of hydrogen chloride and of alcohol[37]; (*b*) the sucroclastic action of nitric acid as influenced by nitrates[38]; (*c*) the hydrolysis of methyl acetate in presence of salts.[39] The argument involved in the first series of experiments is that the diminution of the solubility is due to the combination of the alcohol or hydrogen chloride added with so much of the solvent water, and the consequent reduction of the amount of water available for the solution of the salts. In solutions containing only a small amount of alcohol, however, ammonium chloride is more soluble than in water alone. This is explained by the assumption that a certain amount of the ammonium chloride is unhydrated, and can combine with the alcohol. Assuming that the reduction of solubility was entirely due to this cause, the amount of water combined with the alcohol or hydrogen chloride could be calculated. In this way, the apparent molecular hydration of alcohol was found to vary from about one in the case of ammonium chloride solutions to about four in the case of solutions of potassium chloride; in the case of hydrogen chloride, the variations were somewhat greater. As the amount of alcohol or of hydrogen chloride is increased, the apparent hydration diminishes.

The second method employed by Armstrong for the determination of the degree of hydration of salts in solution depends on the assumption that the effect of a neutral salt on the sucroclastic action of an acid is due to its withdrawing so much of the water, and therefore concentrating the solution. The salts employed were silver nitrate, ammonium nitrate, potassium nitrate, sodium nitrate, lithium nitrate, strontium nitrate, and the average composition of the hydrates of these salts was found to be 5, 7, 8, 11, 13, and 18 molecules of water to one molecule of salt respectively. When the hydration of the salts is measured by their influence on the hydrolysis of methyl acetate, it is found that in the case of the nitrates, more especially, the degrees of hydration obtained are very much less than those calculated from the influence of the salts on the sucroclastic action of the acid. This is explained by assuming that the salts combine with the ester and so prevent to some extent the association of ester and water, which, according to the author, is the intermediate stage of the process of hydrolysis.

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[37] *Abstr.*, 1907, ii, 848. [38] *Ibid.*, 849. [39] *Ibid.*, 849

Another method which has been employed for the purpose of determining the degree of hydration of salts in solution depends on the influence of dissolved substances on the solubility of sparingly soluble gases in water. In some cases, the absorption of sparingly soluble gases is almost independent of the amount of dissolved substance. In cases where this is not so, hydration is assumed, and the degree of this is calculated from the difference in the absorption. This method has been employed by J. C. Philip,[40] who has obtained for a few salts and for sucrose values for the hydration which agree moderately well with those furnished by the preceding methods.

A method similar to this, depending on the influence of salts in producing the separation into two layers of solutions of partially miscible liquids, has been employed by Smirnoff,[41] and, so far as the order of the hydration is concerned, results have been obtained in harmony with other measurements. Evidence in support of the existence of hydrates in solution has also been obtained from distribution experiments carried out by P. Müller and Abegg[42] and by Smirnoff.[43]

Although, as we have seen above, the influence of salts or other solutes on the course of certain reactions, or on the absorption of gases, may apparently be accounted for with fair consistency on the basis of hydrate formation, this explanation does not seem to be universally applicable. This has been pointed out more especially by Senter.[44] The hydrolysis of sodium chloroacetate by water at 102° is considerably retarded by sodium chloride, whereas the action of potassium chloride is slight, and that of the nitrates is negligible.

[40] *Trans.*, 1907, **91**, 711.

[41] *Abstr.*, 1907, ii, 334.

[42] *Ibid.*, 159.

[43] *Ibid.*, 240.

[44] *Trans.*, 1907, **91**, 460.

In the case of the hydrolysis of sodium chloroacetate by sodium hydroxide, the influence of neutral salts (sodium chloride, potassium chloride, sodium nitrate, and sodium sulphate) appears to be practically identical; all accelerate the reaction. Moreover, some indication of the way in which the neutral salts exert their influence is obtained from the fact that the neutral salts retard, to a greater or less extent, the hydrolysis of sodium chloroacetate by water; they all accelerate the action of alkali on the same salt. This points to an influence of the neutral salts on the hydroxyl ions, and the results are not explicable on the view that salts exercise an influence on the course of reactions in aqueous solution owing to their power of combining with some of the solvent water.

Also, with a view to throwing light on the processes operative in solutions, Holmes[45] has studied the volume changes accompanying solution, and, from the results of these, conclusions have been drawn which differ considerably from those obtained in other ways. The contraction which occurs when the lower members of the alcohols and the fatty acids are mixed with water is found to be dependent on the relative volumes of the mixed liquids, and, in order to explain these contractions, the author assumes that the free path of the liquid molecule is bounded by a spherical surface, the radius of which is constant for any molecule of the same substance at constant temperature and pressure. If two sets of molecules therefore are mixed together, one of which has an attraction for the other insufficient to cause the loss of its own individuality and to form a new compound, they can be regarded as a mixture of electrically charged inelastic spheres, the volume of which is always different from the sum of the initial volumes. On this hypothesis, the author draws the conclusion that the maximum contraction will depend on the difference in radii of the influential spheres, and the nearer this ratio approaches unity the nearer will the maximum difference in volumes approach an admixture of equal molecular volumes. The molecular complexities of any mixture of molecules, therefore, must be given by a comparison of the relative volumes which yield a maximum contraction. In the cases above mentioned, the maximum contraction is found when approximately equal proportions of the molecules, referred to the gaseous state, are mixed together, from which the author concludes that the molecular complexity of water is the same as that of the alcohols and the fatty acids, and that the existence of hydrates is thus excluded from the theory of solutions.

Although the maximum contraction may in the case of different substances occur with mixtures of the same relative proportions, and indicate that these substances have the same degree of aggregation, the actual value of the contraction may differ considerably. This the author attributes to forces of repulsion between the molecules of the same substance, and this force of repulsion would vary with the chemical nature of the substance.

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[45] *Trans.*, 1906, **89**, 1774.

Using the numbers for the molecular aggregation obtained from a study of the points of maximum contraction on mixing liquids, the author has also obtained a relationship which gives some explanation of the intermiscibility of liquids. If one multiplies the molecular volumes of different substances referred to the gaseous state by the degree of aggregation as compared with water, the true molecular volume of the liquid is obtained, and it is found that in most cases the intermiscibility of two liquids is all the greater the nearer these molecular volumes are to one another. This is illustrated by the miscibility relations of ethyl alcohol and of carbon disulphide with water. The molecular volumes of these two substances referred to the gaseous state are nearly the same (3·22 and 3·34 respectively), but the degree of aggregation as compared with water is 1 and 4 respectively. The true molecular volumes are therefore 3·22 and 13·36, and carbon disulphide with the much greater molecular volume is therefore less soluble.

The study of these volume changes on solution has been continued during the past year by Holmes and Sageman,[46] who have sought to eliminate two factors which may have a disturbing influence, namely, the difference in the relative weights of the molecules, which, from the circumstance that there are spaces between the molecules, results in more closely packing, and the difference in the relative volumes or influential spheres occupied by the molecules, which again allows of further closely packing as this difference increases. From the volume changes of mixtures of sulphuric acid and various sulphates chosen so that the influences just mentioned were eliminated as far as possible, the authors conclude that sulphuric acid and the sulphates of potassium, sodium, ammonium, magnesium, zinc, and copper are similarly aggregated in solution, and that the volumetric changes which occur are due to the action of physical forces inherent in the molecules, and are independent of chemical affinity and the formation of acid sulphates, and this conclusion is supported by the marked difference in the volume changes in those cases, for example, neutralisation of an acid by alkali, where the chemical action may be regarded as the chief influence at work. The interpretation of the experiments just described on the basis of the theory advanced by Holmes, leads therefore to the conclusion that hydrates are not formed in solution.

When we review the work which has been carried out during the past year in connexion with aqueous solutions, more especially solutions of moderate or of great concentration, we find that there is a tendency to give greater emphasis to the combination of solvent and solute as explaining the properties of solutions. The theories of osmotic pressure, supplemented by the theory of electrolytic dissociation and the law of mass action, by means of which alone we are enabled to co-ordinate in a quantitative manner the various properties of dilute solutions, even if sometimes in an imperfect manner, are insufficient in the case of more concentrated solutions. Whether this insufficiency arises from some error inherent in the foundations of these theories, or is due to "disturbing factors," the nature and extent of which are at present outside our knowledge, has been, and still is, a subject of debate.

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[46] *Trans.*, 1907, **91**, 1606.

From the preceding sections, we have seen that there is a considerable volume of experimental results which can be interpreted with fair consistency on the basis of hydrate formation, and support for the view that hydrates exist in aqueous solution has also been obtained from a consideration of the thermochemistry of solutions [47] and of equilibrium curves.[48] That hydrate formation occurs in aqueous solution is now accepted probably by the majority of physical chemists, but attention must also be given to the contrary conclusion arrived at by Holmes (*supra*).

During the past year, H. E. Armstrong [49] has discussed the processes operative in solutions on the basis of the experiments already reported, and the main process is judged to be hydration of the solute, this hydration being greater in the case of electrolytes than in the case of non-electrolytes. The main points which the author brings forward in support of the view that solution is essentially a manifestation of chemical affinity, and that the theory of electrolytic dissociation is, not only unnecessary, but erroneous, are the following. Sucrose and esters are hydrolysed in presence of acids and also of enzymes, and in both cases the degree of activity varies with the acid or with the enzyme. Since the selective action of the enzymes can be explained on the basis of combination with the hydrolyte, there is no reason why this explanation should not be extended to the acids. Further, it is found that the activity of an acid as a hydrolysing agent is frequently increased by the addition of its neutral salts, and, as non-electrolytes also sometimes act in the same way, there is no reason to account for the activity of electrolytes by an explanation which is inapplicable to non-electrolytes. Similarly with the precipitation of salts from solution: since alcohol, equally with hydrochloric acid, causes the precipitation of chlorides from solution, the explanation which can be applied to the alcohol, namely, hydrate formation, should also be applicable to hydrogen chloride.

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[47] Bousfield and Lowry, *Trans. Faraday Soc.*, 1907, **3**, 1.

[48] Kremann and Ehrlich, *Abstr.*, 1907, ii, 747; Findlay, *Trans. Faraday Soc.*, 1907, **3**, 31.

[49] *Loc. cit.*

The primary process in solution is, therefore, according to the views put forward by H. E. Armstrong, a combination of solvent and solute. As, however, no regularity in behaviour is observed (compare the behaviour of ammonium chloride as compared with potassium chloride in relation to the precipitating power of alcohol, or the influence of nitrates on the hydrolysis of sugar and of methyl acetate by nitric acid), the author introduces the further assumptions referred to above. In this way, it comes about that for the explanation of a comparatively small number of cases there must be introduced a considerable number of fresh assumptions, and the author finds it necessary to acknowledge the existence in solutions of a great variety of molecular conditions simultaneously: of monadic and polymerised molecules, both in the anhydrous and hydrated states, and, in some cases, of compounds formed by the association of the admixed solutes, and also to recognise that the solvent itself, as well as the dissolved substances, is in a state of continued flux. He considers therefore that "the variables are so numerous that it may be doubted whether it will ever be possible to develop any simple treatment of solutions."

That it will ever be possible to sum up the laws of solution in an equation free from complexity is, indeed, not to be looked for, but from the success which, for example, has attended the application by van Laar of the thermodynamic potential to the quantitative treatment of osmotic pressure, and more especially the equilibrium curves of binary mixtures, the future solution of the problem does not appear hopeless. With regard to the purely hydrate theory which has been advanced, it must be said that so far it is merely in the qualitative, and largely speculative, stage. To the writer of this Report, the weakness of the hydrate theories hitherto advanced is that they involve too many unverifiable assumptions. Thus, we cannot even be sure of the main assumption, that the chief factor in solution is hydration, or combination of solvent and solute, for the simple reason that there is no independent and unambiguous method for quantitatively testing hydration. It is quite true that the degree of hydration calculated from different kinds of experiments on the assumption that hydration is the only or the main factor, is found to be approximately the same in a number of cases. But if we take the case of the absorption of gases, we cannot at all be sure that the influence of dissolved salts is due to the abstraction by combination of a certain amount of the solvent water. Thus it has been found from not a few experiments that the solubility of gases depends on, or runs parallel with, the compressibility of the liquid, and a connexion has also been established between solubility and the internal pressure of the liquid, so that the possibility, in any case, of physical influences must also be taken into account. It is quite true that these physical properties can be assumed to be due to combination of solvent and solute, but the proof of this has not yet been supplied. The parallelism between solubility of gases and compressibility of the liquid has been proved to hold also in the case of the mixtures of organic solvents.[50] Reference may also be made to experiments by G. Hüfner,[51] who finds that the diminution of solubility of nitrogen by a number of organic substances depends on the weight concentration, not on the molar concentration, of the added substance. Beyond the main assumption, also, other *ad hoc* assumptions must be introduced from case to case, according as deviations from the supposed normal behaviour are found, so that a general theory on this basis does, indeed, appear difficult. The further study of solutions, however, on the basis of the hypothesis of hydrate formation, as primary or secondary factor, is certainly very desirable.

Non-aqueous Solutions.

For some years, investigations have been carried out by various workers, and along different lines, for the purpose of ascertaining the laws to which electrolytes are subject in non-aqueous solution, and in some cases these laws have been found to be similar to, in other cases to be different from, those which are valid for aqueous solutions. This inquiry has also been pursued by several workers during the past year.

In the case of sparingly soluble electrolytes in water, it was found by van't Hoff and others that the variation of solubility with the temperature was in harmony with the expression:

$$d\log_e(iC)/\alpha T = q/2iT^2,$$

an expression which depends on the three equations: (1) $PV = iRT$; (2) $i = 1 + (n-1)\alpha$; (3) $\alpha = \Lambda/\Lambda_\infty$. Hitherto, the solubility in non-aqueous solutions had not been examined from the point of view of the above law, but this has now been done by Walden[52] in the course of his studies on organic solvent and ionising media. As a result, it was found that for the solubilities of tetraethylammonium iodide and tetrapropylammonium iodide in different organic solvents, the variation of solubility with temperature could be sufficiently accurately represented by the above expression. The same holds also for potassium iodide when dissolved in ethyl alcohol, acetonitrile, or acetone.

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[50] Ritzel, *Abstr.*, 1907, ii, 740.

[51] *Abstr.*, 1907, ii, 165.

[52] *Ibid.*, 231.

From the change of the dissociation constant of a salt with the temperature, it is also possible to calculate the heat of dissociation of the electrolyte, and Walden [53] has made the determinations and calculations in the case of potassium, tetraethylammonium and tetrapropylammonium iodides in a number of organic solvents with a view to determining the relationship between heat of dissociation and the nature of the solvent. As a result, it has been found that the heat of dissociation is practically independent of the nature of the solvent, provided that the electrolyte exists in each solvent in the same molecular condition, and dissociates into the same ions. But there is a further property which is of importance for the study of solutions, namely, the contraction produced when the electrolyte is dissolved. It was found by I. Traube that the molecular solution volume of an electrolyte in aqueous solution is an additive property, and also that it diminishes with increasing dilution, that is, with increasing dissociation of the electrolyte. This has also been found by Walden [54] to be the case for tetraethylammonium, tetrapropylammonium and potassium iodides in different organic solvents. Moreover, it has been found that a molecule produces by its complete dissociation a diminution in the molecular solution volume of about 13—14 c.c., independently of the nature of the binary salt and of the organic solvent, and this value of the contraction is in agreement with that calculated by Drude and Nernst from the theory of electrostriction, and determined by I. Traube in the case of aqueous solutions.

The investigation of the electrical conductivity of solutions of the alcohols and phenols in liquid hydrogen bromide has been carried out by Archibald.[55] In a few cases of the more dilute solutions, the molecular conductivity increases slightly or remains constant as the dilution increases, but in most cases, and in all the more concentrated solutions, the molecular conductivity decreases rapidly with increasing dilution. This behaviour is attributed to combination between solvent and solute,[56] and it is found that the change of the molecular conductivity with dilution, calculated by means of the expression kv^n, where n is the number of molecules of solute uniting with one molecule of solvent to form the electrolytic compounds, gives values, in the case of the phenols, which vary with dilution in the same way as the molecular conductivity of aqueous solutions of inorganic salts; in the case of the alcohols, however, this expression applies over only a narrow range of dilution.

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[53] *Abstr.*, 1907, ii, 437. [54] *Ibid.*, 734. [55] *Ibid.*, 526.

[56] Compare Steele, McIntosh, and Archibald, *Ann. Report*, 1905, 16.

A similar behaviour has also been found in the case of the solutions of organic acids in liquid hydrogen bromide.[57]

Franklin and H. D. Gibbs, also, have studied the electrical conductivity of potassium iodide, silver nitrate, and other substances in methylamine,[58] and find that the curve of molecular conductivity first rises to a maximum, falls to a minimum, and then rises again. In explanation of this behaviour, they adopt the view of G. N. Lewis and P. Wheeler,[59] that the dissociating power of a solvent is increased by solution in it of a well conducting salt.[60]

Ionisation.

The theory of electrical conductivity in solutions has been examined mathematically during the preceding year by Sutherland,[61] who has previously pointed out that account must be taken of the dielectric capacity of the solvent and of the ions. It is now shown that the ionisation of all ordinary solutions at all strengths is complete. The fraction currently called the degree of ionisation really originates in a resistance which the ions offer to one another's motion because of their forming with the solvent, through their electric action on one another, a medium which offers a special viscous resistance to the motion of each individual ion. This is one new type of viscosity of electric origin. But the charge of each ion causes electric induction through the surrounding solution, and with this is associated a second new type of viscosity, also of electric origin. These, with the ordinary viscosity of the solution, give three resistances to the motion of an ion. When the sum of these is equated to the electric driving force, a formula for the molecular conductivity is obtained which is found to be in harmony with the experimental results obtained with non-aqueous and with aqueous solutions both at the ordinary and at higher temperatures. In view of this result, the author believes that the current theory of solutions will have to be re-written. The idea of partial ionisation, whilst it can give a formal qualitative account of the chief phenomena of solutions, being, as the author believes, dynamically wrong, cannot furnish a correct quantitative correlation of their properties. The weak acids which follow the Ostwald dilution law, and also the electrolytes which can ionise in two or more different ways, for example, sulphuric acid, are exceptions to the above treatment.

In opposition to the current views regarding the free existence of ions, H. E. Armstrong[62] puts forward the view that the increase in the molecular conductivity which accompanies dilution is probably due to the gradual breaking up of the more or less polymerised salt molecules into simple molecules or monads. These electrically effective monads are probably hydrated or hydroxylated, and the process of electrolysis is regarded as taking place after the manner represented by the theory of Grotthus.

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[57] *Abstr.*, 1907, ii, 840.

[58] *Ibid.*, 840.

[59] *Ann. Report*, 1906, 19.

[60] Compare Shinn, *Abstr.*, 1907, ii, 926, who obtains somewhat similar results in the case of ethylamine solutions.

[61] *Abstr.*, 1907, ii, 599.

[62] *Ibid*, 850.

The ionisation of water at 0°, 18°, and 25° has been determined by Kanolt[63] from measurements of the hydrolysis of the ammonium salt of diketotetrahydrothiazole. The values of the dissociation constant so obtained are: 0°, $0{\cdot}089 \times 10^{-14}$; 18°, $0{\cdot}46 \times 10^{-14}$; 25°, $0{\cdot}82 \times 10^{-14}$. These values are lower than those obtained by Kohlrausch and Heydweiller from direct measurement of the conductivity of pure water.

Passivity.

The problem of the passivity of metals, and more especially of iron, is one which has now for very many years engaged the attention of chemists, and not a few explanations of the phenomenon, both physical and chemical, have been advanced. In spite of a large amount of experimental work carried out in recent times, a final solution of the problem has perhaps not yet been reached, although the opinion which seems now to be most probable is that it is due to the formation of a layer of ferroso-ferric oxide. This opinion is, however, by no means unanimous.

The subject of the passivifying of iron, and of the activifying of passive iron, has been very fully investigated by Heathcote,[64] who has studied, not only the chemical nature of solutions which bring about passivity and activity, but also the electrometric state of the metal in the two states. As passivity does not appear to be a static phenomenon, not a few of the conflicting results obtained by previous workers are attributed to differences in the degree of passivity, and to the employment of different standards of passivity. According to the author, iron is regarded as passive when, after plunging in nitric acid, of sp. gr. 1·2, shaking for a moment in the acid, and then holding motionless, no chemical action can be detected at the surface by the unaided eye, the temperature of the acid being about 15—17°. Passivification can be produced, not only by immersion of the metal in certain solutions, but also by the electric current, and a close connexion has been found to exist between the phenomena observed in the two cases. The author therefore believes that the process of passivification is in all cases electrolytic, and that, when no external current is employed, current is generated between one part of the surface and another. From this standpoint, the process of passivification is pictured in the following manner. When iron is immersed in a solution, some of the metal passes into solution, forming ferrous ions, or the ferrous ions in the metal pass into the solution from all parts of the surface. The solution pressure of the iron will not, however, be the same at all points of the surface, but will be greater, for example, at the ridges and points than at the hollows on the surface. There will therefore arise local currents, and, if the solution will act as a depolariser at the cathode of these local circuits, the current may persist until passivification at the anodes of the local circuits is effected. This process may require a shorter or longer time, according to the depolarising power of the solution at the cathode and its chemical action on the active iron. If the rate of action of the solution on the passive particle is small, and if the solution can depolarise, currents between the passive and active parts may passivify the active areas, and passivity may thus be established over the whole surface. Since, however, the resistance to an electric current from or to a point is infinite, so this point will probably never become really passive. Likewise, the bottoms of crevices or of pits on the surface will remain active. So long as these exist, they will give rise to currents, while the metal remains passive. Passive iron is soluble, but these active particles will generate current sufficient to maintain it in the passive condition so long as the liquid will continue to combine with the electrolytic products and prevent the activification of the passive part. If the depolarisation fails, the activity will spread from the active areas.

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[63] *Abstr.*, 1907, ii, 839.

[64] *Ibid.*, 851.

The phenomena of passivity are, according to the author, best explained on the assumption of the formation of a layer of magnetic oxide. The hydroxyl ion can be liberated even from solutions which contain no oxygenated anions, and the results obtained go to show that it is the hydroxyl ion which effects passivity, and that this state is due to the formation of a solid phase. This view of the cause of passivity is also borne out by the *E.M.F.* measurements of Haber and Maitland.[65] It is, however, opposed by experiments by W. J. Müller and J. G. Königsberger.[66] These investigators measured the reflecting power of iron mirrors immersed in alkaline solutions both in their natural condition and when polarised anodically and cathodically. Although *E.M.F.* measurements showed that the metal was sometimes in the active and sometimes in the passive state, the reflecting power was always the same. This result is taken as proving that the passive state is not due to the formation of a layer of oxide.

The writer believes, however, that some objection might be taken to the conclusiveness of the argument on the grounds that, whilst a film of about molecular dimensions might be sufficient to give rise to the potential of passive iron, it would require to have a thickness of the order of a wave-length of light in order to affect the reflecting power.

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[65] *Abstr.*, 1907, ii, 598.

[66] *ibid.*, 924.

The phenomenon of passivity has also been observed in the case of a gold anode in solution of commercial potassium cyanide (containing sodium cyanide), and this passivity appeared to be due to the formation of a less soluble film of sodium gold cyanide.[67]

Electro-chemistry of Alloys.

The influence on the electrical conductivity of the addition of one metal to another has long been known, and the insight into the nature of alloys which has been obtained in recent years, chiefly by thermal and microscopic methods, allows of a fuller knowledge being obtained of the relations existing between the electrical conductivity and the nature of the alloy. Guertler[68] has, during the preceding year, collated the available data relating to this problem, and has formulated the relationships which he has found to obtain in the following rules: (1) When the electrical conductivity of the alloys is a linear function of the volume concentration of the two constituent metals, the latter do not form solid solutions to any notable extent (not exceeding 0·05 per cent.); the converse rule also holds. This is found, for example, in the case of tin and lead, cadmium and zinc, &c. (2) The electrical conductivity of alloys which form a continuous series of mixed crystals, follows a smooth curve with a low minimum, and conversely. This is met with, for example, in the alloys of gold and silver, copper and nickel. (3) If the formation of solid solutions is only a limited one, the first rule applies for the parts of the curve between the concentrations of the saturated mixed crystals (for instance, the rule applies to the saturated mixed crystals as to pure metals), and the second rule applies to the concentrations between the pure metals and the saturated mixed crystals. Such conditions are met with in the case of copper and silver. (4) If in a series of alloys of two metals there exist m compounds, then the conductivity curves can, like the thermal equilibrium curves, be divided into $m+1$ binary diagrams, controlled by the first three rules. It follows therefore that, from the form of the electrical conductivity curve, information can be obtained regarding the existence or otherwise of compounds, and, generally, of the nature of the alloys. Whereas, in the case of the conductivity curve, a peak indicates the existence of a compound, the absence of a peak does not necessarily indicate the absence of compounds. As showing the reliability of the conductivity curves for the detection of the formation of compounds, the following few cases may be cited:

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[67] Coehn and C. L. Jacobsen, *Abstr.*, 1907, ii, 926.

[68] *Abstr.*, 1907, ii, 65.

Series of alloys.	Compounds indicated by	
	Thermal or microscopic examination.	Conductivity.
Gold-Tin	$AuSn$	$AuSn$ (probable).
	$AuSn_2$	$AuSn_2$ (proved).
	$AuSn_4$	$AuSn_4$ (probable).
Copper-Tin	Cu_4Sn	Cu_4Sn (proved).
	Cu_3Sn	Cu_3Sn ,,
	$CuSn$	$CuSn$,,

In all cases, it is found that the conductivity curve for a series of alloys lies below the straight line joining the conductivities of the pure components.[69]

Moreover, it has been found[70] that similar relationships hold between the concentration and the temperature-coefficients of conductivity, and, consequently, the latter can also be used for the elucidation of the nature of alloys.

The study of the electrical potential of alloys in contact with an electrolyte has also been subjected to re-investigation by Pushin[71] as a means of determining the nature of alloys. In the case of a cell of the general arrangement $M_1 \mid M_1X \mid M_1 + M_2$, where M_1 and M_2 are two metals, and M_1X a solution of a salt of the less noble metal, M_1, the potential curve which is obtained with varying proportions of M_1 and M_2 will depend on the nature of the alloy. When the two metals form neither solid solutions nor compounds, the potential of the mixture will be the potential of the less noble metal, M_1, and therefore the cell will show no *E.M.F.* Where a solid solution is formed, the *E.M.F.* curve will be a continuous one, varying between the potential of M_1 and of M_2. When a compound is formed, this will have its own potential, and, consequently, its formation will be evidenced by a sharp break in the *E.M.F.* curve. Combinations of these three types can also occur according to the solubility relations of the metals in the solid state, and to the number of compounds formed. A number of cases have been examined experimentally, and, although the method had been used by others and considered to be rather untrustworthy, the author demonstrates, in a number of cases, at least, the applicability of the method.

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[69] See also Kurnakoff and Schemtschuschny, *Abstr.*, 1907, ii, 525.

[70] *Abstr.*, 1907, ii, 524.

[71] *Ibid.*, 325.

Metastable State.

The conditions under which spontaneous crystallisation of supercooled liquids takes place has been studied by several investigators during the past year, but the exact factors influencing the existence of metastable liquids have not yet been completely elucidated. S. W. Young and W. E. Burke [72] have studied the crystallisation of supercooled *p*-nitrotoluene, which had been maintained for definite periods of time at temperatures 10° and 30° respectively above the melting point of the solid. It was found that the longer the substance is heated and the higher the temperature to which it is heated, the less readily does crystallisation occur. The effect of the prolonged heating at higher temperatures is to a certain extent lasting; a sample of the substance which has been so treated does not show the same readiness to crystallise (after solidification and re-melting) as a sample which has not been so treated. If the substance is kept for a considerable time in the solid state, the "sterilisation" is favoured. While it seems possible by means of the nuclear hypothesis to explain the influence of the time and temperature of heating, this is not so in the case of the influence of the time in the solid state. The effect of heating at higher temperatures has also been studied by de Coppet,[73] who also finds that shaking does not induce crystallisation in the supercooled liquid.

In the case of binary mixtures, Miers and Miss Isaac [74] have extended their previous work [75] by a study of the conditions of crystallisation in various mixtures of phenyl salicylate (salol) and β-naphthyl salicylate (betol). The normal freezing point curve of mixtures of these substances is a two-branched curve with a eutectic point at a composition of 78 per cent. of salol. The supersolubility curve is found to run almost parallel with the freezing point curve, but the interval between the two curves is less on the side of pure salol than on the side of betol. It follows from this that the point of intersection of the two supersolubility curves, called by the authors the hypertectic point, does not represent the same composition as the eutectic point. These conditions are represented by the accompanying diagram.

With the help of this diagram, it is easy to explain the different crystallisations which can occur in binary mixtures, more especially in those cases where artificial inoculation and stirring does not take place as in the natural crystallisation of rocks. On cooling a mixture of the two components, crystallisation and slow growth of one of the components can occur on inoculation when the temperature passes the freezing-point curve. The dense shower of fine crystals, however, will make its appearance only after the curve of supersolubility is reached. Since, as we have seen, the composition at the eutectic point may not be the same as at the hypertectic, it follows that from the eutectic mixture, on cooling, the one component may separate out in the dense, labile shower before the other, and, consequently, the fine-grained, eutectic conglomerate will not be obtained.• On the other hand, it will be observed that the

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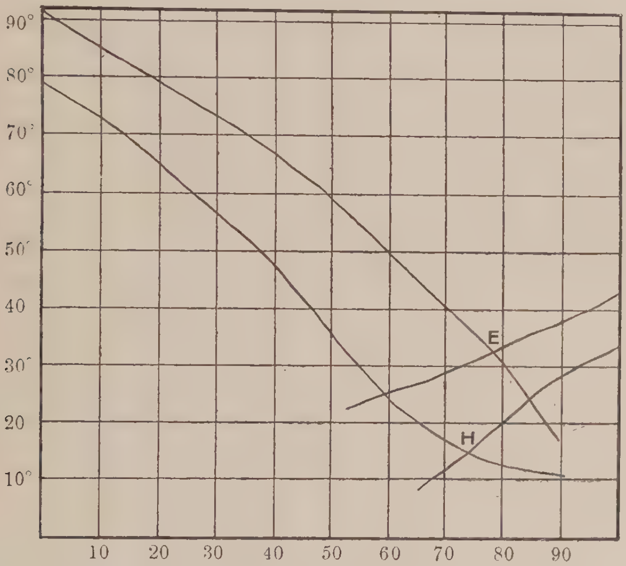
[72] *Abstr.*, 1907, ii, 433.

[73] *Ibid.*, 335.

[74] *Ibid.*, 670.

[75] *Ann. Report*, 1906, 27.



Per cent. salol.

liquid which, under normal conditions, may be expected to yield the eutectic structure is that of which the composition corresponds with the hypertectic point, *H*. By reason of the suspended transformations which may occur, and which are indicated by the prolongation of the curves beyond the points of intersection, a binary mixture can, on cooling, exhibit several freezing points. Thus, for example, a mixture consisting of 90 per cent. salol and 10 per cent. betol yielded crystals of salol by inoculation at 38°, a labile shower of salol at 28°, crystals of betol by inoculation when supercooled to 17·5°, and a labile shower of betol when supercooled to 10·5°.

Colloids.

Classification of Colloids.—The classification of colloidal solutions on the basis of their heterogeneity has been discussed by Wolfgang Ostwald.[76] From ordinary heterogeneous systems, the colloidal solutions are distinguished as being "disperse" heterogeneous (or microheterogeneous). It is not so much the smallness of the particles as the large surface development in a given volume that is characteristic of the colloidal solutions. In the case of two-phase systems, there are, as a rule, an incoherent more or less mobile disperse phase, and a coherent "dispersion medium." For systematic purposes, it is not advantageous to employ maximum or minimum values of the surface, since there are all gradations between ordinary heterogeneous systems and colloidal solutions, but we can employ, as the basis of classification, the number of phases and the physical state both of the disperse phase and of the dispersion medium. Thus, for example, when we have a liquid dispersion medium, we may have a solid, liquid, or gaseous disperse phase, yielding suspensions, emulsions, and foams respectively.

With regard to the precipitation of colloids from solution, and the osmotic pressure of colloidal solutions, the results of a large number of experiments have been published by Duclaux.[77] With regard to the precipitation of colloids by salts, the author points out, first of all, that the stability of a colloid is increased by the presence of electrolyte derived from the method of preparation, and that the amount of electrolyte required to precipitate the colloid is frequently equal to the amount present as impurity. As the colloid is freed from the electrolytic impurity, the amount of salt required to cause precipitation is diminished, that is, the solutions become less stable.

On measuring the osmotic pressure of colloidal solutions against the intermicellar fluid (instead of against water), it was found that the osmotic pressure tended to a maximum value corresponding with the maximum concentration which the colloidal solution can attain. On passing beyond this limiting pressure, the colloid solidifies or condenses. This solidification, the author regards as the consequence of too great approximation, and not of a change in the chemical composition, and the osmotic pressure, as well as the Brownian movement, is regarded as due to the electrostatic repulsions of their charges together with the charges on the ions of the intermicellar liquid. The solidification of the solution, or the agglomeration of the colloidal material, is due to the stoppage or retardation of the Brownian movement, due to the accumulation of charges round each micella. By means of this hypothesis, the author explains, in a qualitative manner, the varied behaviour of colloidal solutions with regard to precipitation and osmotic pressure.

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[76] *Abstr.*, 1907, ii, 939.

[77] *J. Chim. phys.*, 1907, **5**, 29.

The osmotic pressure of colloidal solutions, more especially as influenced by the presence of electrolytes, has also been measured by Lillie,[78] who found that, in the case of solutions of egg-albumin, the osmotic pressure is depressed by salts, the degree of action depending on the ions. The presence of non-electrolytes has little or no effect.

With regard to the stability of colloidal solutions, it is pointed out by Svedberg[79] that neither Perrin's rule, that the stability depends on the dielectric constant of the medium, nor Burton's rule, that charged hydrides or hydroxides are formed by combination, holds in the case, at least, of solutions of colloidal platinum in various organic media. The viscosity, however, of the medium is of especial importance. According to Billitzer,[80] the stability depends on the density of the suspended particles and of the medium, on the relation between the friction to be overcome on precipitation and the gravitational forces, and on the magnitude and constancy of the opposite electric charges. Since the last-mentioned factor depends on the dielectric constant of the medium, the stability will partly depend on this, but the author agrees with Svedberg in the conclusion regarding the invalidity of Perrin's and Burton's rules.

Alex. Findlay.

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[78] *Abstr.*, 1907, ii, 607. [79] *Ibid.*, 535. [80] *Ibid.*, 535.

INORGANIC CHEMISTRY.

Although there has been a considerable output of interesting and important work, there is again nothing of a very novel or startling character to record with regard to the progress of Inorganic Chemistry during the period covered by the present Annual Report. No new element, or pure compound of a new element, has been isolated, although indications have been obtained of the existence of a hitherto unknown constituent in the rare-earth series. The transmutation of the elements, if placed beyond all doubt, would, of course, be of much greater interest and importance than the mere discovery of new elements to fill up recognised blanks in the periodic system; but, whatever be the ultimate result of Sir Wm. Ramsay's work in this connexion, the matter has not yet reached a stage which calls for its being treated in a part of the Report dealing purely with inorganic chemistry as usually understood.

The year's work has followed pretty closely along previously established lines; considerable use has been made of the facilities provided by modern chemical equipment and methods. The easy attainment of high temperatures by means of electric furnaces, &c., has led to a greatly extended study of compounds such as carbides, silicides, borides, &c., of alloys of the metals, and of mixtures more or less analogous to these.

One can hardly mention the matter of high-temperature research without referring to the great loss which befell this branch of inorganic chemistry by the death of Henri Moissan early in the year, for he was a pioneer in such work.

In the other direction, there has also been a fair amount of low-temperature work, although to nothing like the same extent. It is evident, however, that liquid-air machines, as well as electric furnaces, are becoming more and more part of the ordinary equipment of a chemical laboratory, with great advantage, even to the worker who does not wish to reach the extreme limits of practicable temperatures, but who, nevertheless, occasionally finds it highly desirable to work at temperatures well outside those ordinarily obtainable. The great improvements which have recently been effected in the preparation of pure silica-ware, and the cheapening of the cost, have also placed a new power within the reach of chemists generally.

The study of the "rare earths" is another fairly well-defined branch of work which has been steadily developed during the year, and in which considerable progress has been made; the same is the case in connexion with the investigation of numerous "complex" salts, such as the ammonia derivatives of the cobalt and platinum metals, various chromium derivatives, &c. Werner, whose name is so intimately associated with the recent advancement of our knowledge concerning complex salts, has been extending his theoretical conclusions, derived from his studies of these compounds, more and more into the region of the simpler salts, and his recent papers dealing with these matters are very interesting and suggestive.

Revision of Atomic Weights.

The recently obtained values for the atomic weight of nitrogen are discussed by D. Berthelot,[1] who considers that they amply confirm the values 14·007 and 14·000 obtained by him ten years ago.

The revision of the combining weights of various elements, which has in recent years been so admirably carried out by T. W. Richards and his co-workers, is being continued. The atomic weight of silver has been determined, in conjunction with G. S. Forbes,[2] by the synthesis of silver nitrate; in four out of six experiments, the ratio $Ag : AgNO_3$ was found to be 100 : 157·480, and in the remaining two, 100 : 157·481. The value for silver to be deduced from these results, of course, depends on what value is accepted for nitrogen; if this is taken as 14·037 (for an upper limit), then Ag = 107·930, whilst if it be taken as 14·008 (for a lower limit), then Ag = 107·880.

Richards and G. Jones[3] have obtained revised values for sulphur and chlorine by the conversion of silver sulphate into chloride. Ten experiments gave, as an average result for the ratio $Ag_2SO_4 : AgCl$, the value 100 : 91·933, the extremes being 91·929 and 91·936. Here, again, the values for the atomic weights, to be deduced from this result, depend on the value adopted for nitrogen, since the value for silver is involved. Corresponding with the limits stated in the preceding paragraph, the limits for chlorine are 35·473 and 35·457 respectively, and those for sulphur are 32·113 and 32·069. The last value is the one which most closely agrees with that deduced from the more recent work on gas densities.

The revision of the atomic weight of potassium has been carried a stage further; as mentioned in last year's Report, Richards and

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[1] *Abstr.*, 1907, ii, 680.
[2] *Ibid.*, 685.
[3] *Ibid.*, 685.

Stähler, working on pure potassium chloride, obtained the value K = 39·114, adopting the value Ag = 107·93. Richards and E. Mueller[4] have now published the results of similar work performed on pure potassium bromide. Four determinations gave the mean value of 100 : 63·373 for the ratio AgBr : KBr, and ten determinations gave the mean value 100 : 110·319 for the ratio Ag : KBr. These give respectively the values 39·1135 and 39·1143 for the atomic weight of potassium (Ag = 107·93 as before).

From all the various series of determinations, Richards concludes that K = 39·114 may be taken as the probable value, assuming Ag = 107·93, Br = 79·953, Cl = 35·473; O = 16 serves as the basis throughout. The close agreement obtained in the two investigations indicates a high degree of accuracy for the values for chlorine, bromine, and silver, relatively to one another.

P. A. Guye and Ter-Gazarian[5] have checked the value for the atomic weight of chlorine by accurate determinations of the density of hydrogen chloride. For this purpose, the gas was prepared from sodium chloride and sulphuric acid, dried by sulphuric acid and phosphoric oxide, liquefied, and fractionally distilled. The weight of one litre was found to be 1·6398 under standard conditions (Leduc's value is 1·6409); this gives Cl = 35·461.

The questions whether or not tellurium is a homogeneous element, and, if so, what is the correct value to adopt for its atomic weight, have been the subject of an important investigation by H. B. Baker and A. H. Bennett.[6] Eight different methods of fractionation were employed, and in no single case could any difference be detected between the first and the last fractions, other than what fell within the limits of experimental error. The following were the methods applied fractionally: (1) Crystallisation of telluric acid; (2) Dissolution of barium tellurate; (3) Distillation of tellurium; (4) Distillation of tellurium tetrachloride; (5) Distillation of tellurium dioxide; (6) Decomposition of tellurium hydride; (7) Electrolysis of tellurium tetrachloride and tetrabromide; (8) Precipitation from solution of tellurium tetrachloride by addition of water.

For the purpose of testing most of the fractions, they were converted into dioxide, and the percentage of oxygen in the samples of dioxide was determined by reduction with sulphur in an ingenious manner devised by Berzelius, and employed by him in determining the equivalent value of arsenic; the method consists in heating the dioxide with sulphur in an apparatus so arranged that nothing but sulphur dioxide can escape. The other method adopted was to convert the fractions into tellurium, and then determine the proportion of tetrabromide obtained from this.

[4] *Abstr.*, 1907, ii, 615. [5] *Ibid.*, 80. [6] *Trans.*, 1907, **91**, 1849

The average percentage of oxygen in the dioxide was thus found to be 20·048 ($O=16$, $S=32·06$), and of tellurium in the tetrabromide, 28·518. The value for the atomic weight deduced from these results is consequently: by the first method, $Te=127·609$; by the second, $Te=127·601$ ($Br=79·96$). The probable value is taken as 127·60.

Since the tellurium employed was in some cases of widely different origin, the results of the investigation may be taken as conclusive of the homogeneity of the element, and confirm the relative positions of iodine and tellurium as regards order of atomic weight.

Several years ago, an investigation by Thiel led to a considerable increase in the accepted value for the atomic weight of indium. This is confirmed by F. C. Mathers,[7] who analysed the trichloride and the tribromide, prepared by passing dry chlorine gas or dry bromine vapour over the metal, and subliming the product in each case. These methods not only gave consistent results throughout each series of five experiments, but the two values found by them agree well with each other; they were 114·88 and 114·86. The value $In=114·9$ may therefore be accepted ($Ag=107·92$; $Br=79·955$; $Cl=35·47$).

Several determinations of atomic weights will be referred to incidentally in connexion with the rare-earth group.

G. D. Hinrichs[8] discusses the "absolute" atomic weight of a number of elements which have recently been investigated by various workers; he urges the adoption of the following round numbers as being the true atomic weights of the elements indicated: $C=12$; $Cl=35·5$; $Mn=55$; $Br=80$; $Ag=108$; $Dy=162·5$.

Rare Earths.

As already indicated, there have appeared during the year a considerable number of papers, some of them long memoirs, dealing with the substances generally included under this heading. Many of these are the result of a vast amount of careful and laborious work, involving the preparation of scores, or even hundreds, of fractions, and repeated examination of the products thus obtained.

One of the chief aims of workers in this field is, of course, to obtain better modes of fractionation, by discovering which salts show the greatest differences of solubility in various solvents, and various new processes have been suggested. A very extensive memoir on the preparation of pure neodymium oxide, and on new methods of separating the rare earths, has been published by O. Holmberg.[9] In this paper, a large number of organic salts of the rare-earth metals are described, principally those derived from benzenesulphonic acid and its nitro-, chloro-, and bromo-substitution products. It was found that the solubilities of the *m*-nitrobenzenesulphonates in many cases are widely different from one another, more so than with other salts, and that therefore improved fractionation could be effected by their means. By repeatedly working up the impure neodymium salt, it was found possible to purify it so completely that a series of the various later fractions yielded material exhibiting a constant result for the atomic weight (the oxide-sulphate method being used). The average result of several concordant sets of atomic weight determinations gave the value Nd = 144·08. The method was also found to work well for the purification of samarium oxide, yielding a constant material, for which the atomic weight value Sa = 150 was obtained. It did not yield good results for the preparation of pure gadolinium oxide, however, but in this case a satisfactory method of separation from terbium was found in dissolution of the material in picric acid and fractional precipitation with ammonia. From this material, the atomic-weight value Gd = 156 was obtained.

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[7] *Abstr.*, 1907, ii, 352.

[8] *Ibid.*, 90, 450, 622, 679.

[9] *Ibid.*, 90.

C. A. v. Welsbach[10] has devoted attention chiefly to the isolation, in a satisfactory degree of purity, of the members of the ytterbium group. The method which he adopts is first to obtain them together in the form of basic nitrates, and then to fractionate them by conversion into double ammonium oxalates and crystallisation of these from saturated aqueous solution of ammonium oxalate. The solubilities of the double salts in this solvent vary very considerably; for example, the solubility of the ytterbium compound is ten times greater than that of the holmium compound.

According to Langlet,[11] the best method of separating holmium from erbium and ytterbium, provided the latter is not present in large quantity, is by fractional crystallisation of the chlorides from solution in hydrochloric acid of constant boiling point. As regards the testing of the rare earths for purity, he holds that the generally accepted criterion of constancy of value found for atomic weight is not trustworthy by itself, since he finds that such constancy is not always associated with constancy of absorption spectrum. Urbain[12] states that by the oft-repeated fractional crystallisation of ordinarily pure "ytterbium" nitrate from solution in nitric acid of density 1·3, he has obtained end fractions which exhibit lower and higher atomic weight values (169·9—173·8); those of low atomic weight show arc-spectrum lines which are to be attributed to thulium, whilst those giving the higher values show well-marked lines which must be ascribed to a new element, "lutecium." Rejection of those lines which come into prominence in the end fractions leaves the spectrum of ytterbium proper, "neoytterbium." Lines which did not coincide with those of any known element were also obtained by von Welsbach (*v. sup.*) in some of his fractions.

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[10] *Abstr.*, 1907, ii, 26.
[11] *Ibid.*, 955.
[12] *Ibid.*, 956.

A new method for the separation of yttrium earths is described by C. James[13]; the oxalates are dissolved by warming with a saturated solution of ammonium carbonate in dilute ammonium hydroxide, and fractional precipitation is effected by boiling the solution. It is claimed that by this method a rapid separation of erbium from holmium, &c., can be effected. Work in this group has also been carried out along recognised lines by A. Bettendorff,[14] and by V. von Lang and Haitinger[15]; the latter give crystallographic descriptions of some of the compounds examined.

Cerium compounds have received a considerable amount of attention. The question as to the position of this element in the fourth group of the periodic system, in view of its apparent tendency to form tervalent rather than quadrivalent derivatives, is discussed by G. A. Barbieri, who also describes new methods of preparing ceric salts.[16] He is of the opinion that cerous compounds are more stable than ceric only in cases where cerium constitutes the cation; whenever complex anions containing cerium can be formed, then there is a ready change from the cerous to the ceric condition. A large number of cerous salts, especially those of organic acids, have been prepared by G. T. Morgan and E. Cahen,[17] and a lengthy paper dealing with cerium compounds generally has been published by Wyrouboff and Verneuil.[18]

A matter of considerable practical interest is dealt with by R. J. Meyer and A. Anschütz,[19] who have sought to obtain from the chemical side some indication as to the correctness or otherwise of the explanations which have been put forward for the high emissivity of the incandescent Auer mantle. An interesting point noted by them is that when the dioxides of thorium and cerium are heated together, no loss of weight can be detected, but, if the resulting material is mixed with potassium iodide and hydrochloric acid and then distilled, less iodine is obtained than would have been the case with the original cerium dioxide. It was found that thoria could thus render inert about 7 per cent. of cerium dioxide, so presumably the 1 per cent. which is added to Auer mantles is all in the peculiar condition indicated above. The authors point out, also, that, when cerium nitrate is heated alone, the residual oxide contains more oxygen than corresponds with CeO_2, and may even approach what is requisite for CeO_3.

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[13] *Abstr.*, 1907, ii, 467.

[14] *Ibid.*, 172.

[15] *Ibid.*, 204.

[16] *Ibid.*, 466, 467.

[17] *Trans.*, 1907, **91**, 475.

[18] *Abstr.*, 1907, ii, 26.

[19] *Ibid.*, 557.

For the preparation of cerous salts from cerium dioxide, Marino[20] recommends treatment with the appropriate acid in presence of quinol, which acts as a reducing agent; the method may even be used as a means of effecting the separation of cerium and thorium, on account of the latter not being easily brought into solution in the form of its ignited dioxide.

For the preparation of the metals of the rare earths, for example, cerium, Muthmann and others[21] recommend the electrolysis of solution of the oxide dissolved in the fluoride of the metal; other fluorides, such as cryolite, potassium fluoride, or calcium fluoride, do not give satisfactory results.

The Argon Group.

Moureu and Biquard[22] have examined the gases extracted from a large number of mineral springs. For the determination of the rare gases present, the chemically inactive residues were submitted to fractionation by Dewar's method of absorption in wood charcoal at low temperatures. The principal ingredient was found to be helium, which varied greatly in amount in the different cases, from a minimum of 0·00063 per cent. of the total gases in the Châtel-Guyon spring, to a maximum of 5·34 per cent. in that of Maizières (the waters of which also contain krypton); the quantities of neon present were too small to be separated. The proportion of helium occurring in the natural gas of various wells in America has been determined by Cady and McFarland[23]; in forty-one samples, it was found to vary from merely a trace up to 1·84 per cent.

According to Coates,[24] there are no lines observable in the spectrum of the residue of light gas fractionated from more than 70,000 litres of air other than those due to helium, neon, and hydrogen; there seems therefore to be no reason to assume the existence in air of any rare gas having a density less than that of helium. His results further indicate that the proportion of hydrogen (which, however, it is difficult to determine) is much less than it has been stated to be by some previous observers; it is probably only of the order of one part by volume in one and a half million parts of air.

For the preparation of pure helium from the gases extracted from cleveite, Jaquerod and Perrot[25] take advantage of its ability to pass through quartz at high temperatures. The only other gases by which the quartz is permeable are hydrogen and, possibly, carbon monoxide, and these are easily got rid of by mixing about 5 per cent. of oxygen with the crude helium. The gaseous mixture is introduced into the annular space between a quartz bulb and a platinum cylinder surrounding it, and the apparatus is then heated to 1100°. The bulb is evacuated, and very pure helium diffuses through into the interior. The process, although efficient, is very slow.

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[20] *Abstr.*, 1907, ii, 690.
[21] *Ibid.*, 772.
[22] *Ibid.*, 22.
[23] *Ibid.*, 949.
[24] *Ibid.*, 257.
[25] *Ibid.*, 166.

For the preparation of argon from air, F. Fischer[26] proposes the following method. An iron tube is charged with powdered calcium carbide mixed with 10 per cent. of calcium chloride, after which it is evacuated, and heated to 800°; pure dry air is then admitted into it, whereupon the oxygen and nitrogen are both absorbed, leaving argon.

Group I.

There is comparatively little to report regarding the alkali metals and their compounds generally, beyond what comes more suitably under other headings. The densities of the metals themselves have been determined with great care by Richards and Brink[27] in order to correct the inconsistent values which have hitherto appeared in works of reference. They give the following values for D^{20}: Li, 0·534; Na, 0·9712; K, 0·8621; Rb, 1·532; Cs, 1·87; the last-mentioned is only an approximate value. A liquid alloy of sodium and potassium containing almost exactly 40 per cent. of potassium gave the value 0·919, which is nearly 1 per cent. lower than that calculated from the composition; there is therefore distinct expansion on formation, but it is decidedly less than what occurs when either of the constituent metals fuses.

Until recently, there was very little satisfactory information obtainable regarding the basic oxides of the alkali metals; many of the older statements were known to be entirely misleading, and chemists were left in doubt as to whether or not the oxides could really be prepared pure. The subject has now been placed on a much more satisfactory footing by the publication of the results of investigations by Rengade[28] and by de Forcrand.[29] The work of de Forcrand deals only with lithium oxide; he shows that the methods suggested by Troost (combustion of the metal in oxygen; decomposition of the nitrate by heat; ignition of the carbonate with charcoal) yield impure products only. Lithia can be obtained, however, by dehydration of the hydroxide, LiOH (or its hydrate, $LiOH,H_2O$), by heating in a current of hydrogen to a temperature of about 660—680°; at the lower temperature stated, the process is very much slower than at the upper one, when it is complete in an hour. Lithium carbonate is more easily obtained pure, and forms a more convenient starting point than the hydroxide, for it also can be completely decomposed under the conditions mentioned above; the process is slower, but quantities of carbonate not more than a gram in weight can be converted into oxide in about three hours at 780—800°. The product is a colourless, translucent, fused mass, which is distinctly volatile below 820°.

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[26] *Abstr.*, 1907, ii, 344.

[27] *Ibid.*, 258.

[28] *Ibid.*, 1906, ii, 850; 1907, ii, 83, 457.

[29] *Ibid.*, 1907, ii, 615, 683.

Rengade's work deals with the oxides of the four other alkali metals; his method consists in partly oxidising the particular metal in a current of pure dry oxygen, and then removing the unchanged metal by prolonged distillation in a vacuum at not too high a temperature. He considers it probable that a suboxide is first formed, which decomposes into metal and oxygen.

These oxides are crystalline solids, of density varying from 2·25 (Na_2O) to 4·78 (Cs_2O). Those of sodium and potassium are white when cold, but become yellow when heated; rubidium oxide is pale yellow when cold, and darker when heated; cæsium oxide is red. All of them decompose when heated above 400°, forming the metal and the peroxide. They react with liquid ammonia, forming hydroxide and amide: $M_2O + NH_3 = MOH + MNH_2$. At a temperature somewhat below 200°, they react with hydrogen, forming hydroxide and hydride: $M_2O + H_2 = MOH + MH$. In the cold, they do not react with carbon dioxide, fluorine, chlorine, iodine, or sulphur, but they do so with greater or less readiness when warmed. At the ordinary temperature, cæsium oxide takes fire in hydrogen sulphide; when heated, it unites with oxygen to form the peroxide, Cs_2O_4, and reacts with sulphur dioxide to form a mixture of sulphide and sulphate.

From a study of the absorption of oxygen by rubidium, Rengade[30] describes the formation of the following higher oxides: Rb_2O_2 (yellowish-white); Rb_2O_3 (black); Rb_2O_4 (yellow).

The causticising of sodium and potassium carbonates by slaked lime has been the subject of several investigations; these are chiefly of a physico-chemical nature, and only a few points need be noted here. According to Le Blanc and Novotný,[31] there is no advantage to be gained in the technical process by working under pressure, but attainment of equilibrium may be hastened by efficient stirring, working at a high temperature, and using excess of lime. Wegscheider and H. Walter[32] have studied more particularly the conditions of formation of the double salt, $Na_2CO_3,CaCO_3$, which crystallises out as penta- or di-hydrate and constitutes a source of loss;

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[30] *Abstr.*, 1907, ii, 458.

[31] *Ibid.*, 22.

[32] *Ibid.*, 259, 681, 682.

they confirm the idea that its formation is facilitated by the presence of excess of lime.

"Scheele's process" for obtaining sodium hydroxide direct from chloride solution has been examined physico-chemically by Berl and Austerweil.[33] It depends on the formation of an insoluble basic chloride of lead when salt solution is agitated with litharge, with regeneration of the litharge by means of slaked lime. With *N*-sodium chloride solution, the action is:

$$2NaCl + 4PbO + H_2O = 2NaOH + PbCl_2,3PbO.$$

This basic salt is yellow; a white one, $PbCl_2,4PbO,2H_2O$, is formed with *N*/2 solution. From results obtained in the course of the work, the authors conclude that lead oxide dissolved in sodium hydroxide solution forms the compound $NaHPbO_2$, with some Na_2PbO_2 also if the soda solution is more concentrated than a normal one.

As a method of obtaining pure copper, Vigouroux[34] recommends, first, the preparation of an acid solution of cuprous chloride from copper turnings, and precipitating the salt by filtering into boiled out, but cold, water. The washed material is then decomposed by means of excess of aluminium, used in large pieces; after reduction is complete, the remaining aluminium is picked out, the copper is washed with water, then hydrochloric acid, and again with water; after being dried, it is reduced in a current of hydrogen.

The existence of a peroxide of copper seems to be placed practically beyond doubt by several researches which have been made public. According to Erich Müller and Spitzer,[35] a yellow-coloured peroxide is formed at the anode when a solution of cupric hydroxide in very concentrated sodium hydroxide is electrolysed, or when the sodium hydroxide solution alone is electrolysed with a copper anode; from the loss of copper at the anode, and the deficiency of evolved oxygen with a given quantity of current, they deduce a composition corresponding with the formula Cu_2O_3. L. Moser[36] tried the effect of numerous oxidising agents on various copper compounds, but only with hydrogen peroxide (in 10—30 per cent. neutral solution), acting at 0° on freshly-prepared cupric hydroxide, did he succeed in obtaining a moderately stable peroxide; this was in the form of a brown, crystalline powder. From the determination of the ratio of active oxygen to copper in the moist material (it loses oxygen on drying), he deduces a composition corresponding with a peroxide, CuO_2, but possibly there is also water corresponding with $1H_2O$ (perhaps, therefore, the substance may be really a compound of a lower oxide with hydrogen peroxide). With dilute hydrochloric acid, hydrogen peroxide is regenerated; with concentrated acid, chlorine is evolved. A similar substance is formed transiently when sodium peroxide acts on cupric salt solutions. Erich Müller[37] states that peroxide can also be obtained, as a red solution or yellow precipitate, by acting with chlorine or bromine on strongly alkaline solutions of cupric hydroxide, although Moser was unsuccessful with similar means. By oxidising solutions containing copper and tellurium by means of persulphate in presence of potassium hydroxide, Brauner and B. Kuzma[38] have prepared several copper peroxidic compounds containing tellurium, for example, $2K_2O, Cu_2O_3, 3TeO_3, xH_2O$; they are very unstable.

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[33] *Abstr.*, 1907, ii, 457.

[34] *Ibid.*, 88.

[35] *Ibid.*, 174.

[36] *Ibid.*, 549.

These results show fairly conclusively that there is a copper peroxide, but its exact composition has not yet been quite decisively ascertained.

Although the sulphides of silver and lead show so many striking similarities, they apparently differ entirely from one another as regards their behaviour towards cuprous sulphide at high temperatures; K. Friedrich[39] finds that, after fusion, cuprous sulphide and silver sulphide crystallise together in all proportions, but that cuprous sulphide and lead sulphide crystallise out separately, practically pure, and form a well-marked eutectic mixture.

H. Biltz and Herms[40] have prepared a number of salts of the acid $HCuS_4$. The ammonium salt, which has long been known, is formed when cupric sulphide dissolves in ammonium polysulphide solution, and can fairly easily be crystallised. The potassium, rubidium, and cæsium salts can be prepared from the solution of the ammonium salt by precipitating with the alcoholic solution of the appropriate hydroxide. The salts are dark-coloured and crystalline, and they decompose somewhat readily; various more complex derivatives can be obtained from them.

Evidence as to the molecular weight of cuprous salts has been obtained by E. Beckmann[41] by employing the ebullioscopic method with solutions of cuprous chloride in quinoline; the results show that in dilute solution the molecule corresponds with the formula CuCl, but that in more concentrated solutions there is association to form Cu_2Cl_2. Several other interesting points with regard to cuprous salts, and the relation of the cuprous salts to the cupric salts, have also been published. According to G. A. Barbieri,[42] when cuprous iodide is heated with cupric chloride the following reaction occurs: $2CuI + 2CuCl_2 = 4CuCl + I_2$; similarly with cupric bromide. On the other hand, if cuprous chloride (or bromide) is dissolved in solution of alkali chloride and shaken up with a xylene solution of iodine, the reverse action takes place. Evidently, therefore, the equilibrium $2Cu^{\cdot\cdot} + 2I' \rightleftharpoons 2C^{\cdot} + I_2$ can be displaced through a very wide range, according to the conditions. Guichard[43] finds that the action of anhydrous cupric chloride on hydrogen iodide, $2CuCl_2 + 4HI = 2CuI + I_2 + 4HCl$, takes place even at $-40°$.

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[37] *Abstr.*, 1907, ii, 771.
[38] *Ibid.*, 716.
[39] *Ibid.*, 951.
[40] *Ibid.*, 262.
[41] *Ibid.*, 24.
[42] *Ibid.*, 462.

The formation of cuprous sulphate in solution has been investigated by Foerster and Blankenberg.[44] Copper acts on acid solution of cupric sulphate to form some cuprous sulphate: $CuSO_4 + Cu \rightleftharpoons Cu_2SO_4$; the action is very slight at the ordinary temperature, but increases with rise of temperature. In ammoniacal solution, a corresponding change takes place, and in this case conclusive proof of the existence of the cuprous compound is provided by the formation of a colourless, crystalline compound, $Cu_2SO_4,4NH_3,H_2O$. If the concentration of copper is suitably chosen (not too great), solutions can be prepared which are blue when cold, but become colourless when heated, so that here the influence of temperature can be directly demonstrated. F. Herrmann[45] records an interesting observation closely related to this. If ammonia in excess is added to a solution containing ferrous and cupric sulphates in equimolecular proportions (or preferably with a slight excess of ferrous), the ferrous hydroxide reduces the cupric compound to cuprous, and a colourless solution is obtained, ferric hydroxide being precipitated: $2CuSO_4 + 2FeSO_4 + 10NH_3 + 6H_2O = [Cu(NH_3)_2]_2SO_4 + 2Fe(OH)_3 + 3(NH_4)_2SO_4$. When the mixture is poured into cold dilute sulphuric acid, the original sulphates are regenerated, together with more ammonium sulphate. The reaction provides a good method for preparing ammoniacal cuprous solutions for gas analysis. It is evident from what is here stated that it is useless to employ ammonia as a reagent for cupric salt in presence of excess of ferrous salt.

Apparently cuprous metaphosphate is formed when the acid is fused with excess of copper, hydrogen being evolved, although cupric metaphosphate is found in the crucible after cooling; for if the fused mass is poured off from the unchanged copper and allowed to cool in absence of air, it is found that flakes of copper have been deposited equal in weight to the copper contained in the cupric compound.

The cause of the different colours of colloidal solutions of silver has been investigated by Gallagher,[46] who concludes that the differences are probably due to selective absorption of light, due to varying degrees of coagulation, and depending also on the concentration of the particles in the liquid and on the thickness of the layer. Changes of colour take place only under the influence of light, which probably induces coagulation, and the rate of change increases with increased light intensity. Many organic liquids prevent or retard change, apparently by preventing coagulation.

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[43] *Abstr.*, 1907, ii, 689. [44] *Ibid.*, 89. [45] *Ibid.*, 689. [46] *Ibid.*, 84.

Some interesting results regarding the nature of silver "peroxide," and the existence of the cation $Ag^{\cdot\cdot}$, are published by G. A. Barbieri.[47] By the action of potassium persulphate on silver pyrophosphate, a compound is formed which contains active oxygen and silver in the proportion 1 : 13·12—14·89; it is therefore a derivative of the oxide AgO, which requires the ratio 1 : 13·5. Since apparently it cannot give rise to the formation of hydrogen peroxide, and does not reduce lead peroxide, manganese dioxide, or potassium permanganate in presence of concentrated nitric acid, the oxide AgO is not really a peroxide, but must be looked upon as a basic oxide; as a base, it is weaker than Ag_2O. It can apparently be formed from the latter by means of potassium permanganate in alkaline solution, the following reversible action taking place: $Ag_2O + 2KMnO_4 + 2KOH \rightleftharpoons 2AgO + 2K_2MnO_4 + H_2O$ (or $Ag^{\cdot} + MnO_4{}' \rightleftharpoons Ag^{\cdot\cdot} + MnO_4{}''$). Dissolved in concentrated nitric acid, silver nitrate reduces lead peroxide and bismuth tetroxide, as AgO would appear, in these circumstances, to be a less powerful oxidising agent than these oxides.

Group II.

For the purification of commercial calcium, Muthmann, L. Weiss, and Metzger[48] recommend treatment with absolute alcohol, which dissolves most of the calcium chloride with which the metal is contaminated. A more efficient purification is effected by fusing the metal with calcium chloride-fluoride to a fairly bright red-heat in a closed iron bomb; this product is free from iron and chlorine, and contains about 99·5 per cent. of calcium. The density was found to be 1·41—1·42, which is distinctly lower than that stated by previous observers. In the course of determinations of the heat of combustion in oxygen under pressure, it was found that the lime formed in the bomb had been fused to a clear, glassy mass if the metal was contaminated with chloride to the extent of at least 1 per cent. of chlorine; otherwise, the product was not even sintered.

The use of calcium for the reduction of other elements from their chlorides and oxides is discussed by the above-mentioned chemists, and by F. M. Perkin.[49] In some cases, fairly pure elements can be obtained, but in many the resulting products are alloys, &c. Apart from the latter fact, the method suffers from the drawback that the action is often very violent, and that the lime produced is not fusible at the resultant temperature. Soddy[50] has shown that

[47] *Abstr.*, 1907, ii, 767. [48] *Ibid.*, 767. [49] *Ibid.*, 952. [50] *Ibid.*, 251, 349.

strongly heated calcium is an excellent medium for the separation of the gases of the argon group from mixtures, since all the other gases are completely absorbed by the metal.

Moissan showed that in the preparation of calcium carbide the lime always fuses before the carbide begins to form; Kahn[51] has now found that this is not the case when barium or strontium oxide is heated with charcoal, for at the temperature of melting platinum a product is obtained which, although giving no indications of fusion, nevertheless contains carbide of the metal. He also shows[52] that these carbides, like calcium carbide, act as solvents for carbon, dissolving varying proportions according to the conditions, and depositing graphite on cooling.

The absorption of nitrogen by calcium carbide is found by Polzeniusz[53] to be accelerated considerably by the presence of easily fusible oxygen-free calcium compounds, such as the halides. The same result is obtained by adding the halides of other metals, which react with formation of the calcium compounds; bromides and iodides are, in general, more active than chlorides. When the carbonates of the alkaline earth metals are heated with charcoal in an atmosphere of nitrogen, there is, according to Kühling,[54] a marked difference in the three cases as regards the amount of cyanide and of cyanamide formed. With calcium carbonate at almost 1400°, none of either is formed; with strontium carbonate at above 1200°, the yields are 1·4 and 0·8 respectively; whilst with barium carbonate at almost 1100°, they are 23·4 per cent. and 1·6 per cent. The yields are improved by the addition of chloride to the mixture.

As mentioned in last year's Report, calcium hydride, under the name of *hydrolite*, is now a commercial product, and its use for the preparation of hydrogen is suggested. According to Prats Aymerich,[55] the material, when treated with water, yields about 100 c.c. of gas per gram (about $1\frac{1}{2}$ cub. ft. per lb.); the hydrogen is free from ammonia and acetylene. Although the residual lime does not give any indications of a phosphide when tested, there is a spontaneously inflammable gas evolved when it is dissolved in hydrochloric acid.

The formation of crystallised double carbonates of calcium and the alkali metals has been investigated by Bütschli[56]; in addition to gaylussite, $Na_2CO_3,CaCO_3,5H_2O$, he has prepared the compounds $Na_2CO_3,CaCO_3,2H_2O$, $K_2CO_3,CaCO_3$, and $3K_2CO_3,2CaCO_3,6H_2O$. The formation of sodium calcium carbonate takes place readily from a solution of sodium carbonate with amorphous calcium carbonate;

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[51] *Abstr.*, 1907, ii, 460.
[52] *Ibid.*, 166.
[53] *Ibid.*, 867.
[54] *Ibid.*, 166.
[55] *Ibid.*, 543.
[56] *Ibid.*, 544, 616.

it takes place to a slight extent only with aragonite, and scarcely at all with calcite in the course of thirty-six hours. The author uses these differences for discriminating between the varieties of calcium carbonate deposited in animal tissues.

Several interesting points connected with the process of the setting of plaster of Paris have been discovered by W. A. Davis.[57] He shows that in addition to gypsum, $CaSO_4,2H_2O$ (monoclinic), the semihydrate, $CaSO_4,\frac{1}{2}H_2O$, soluble or quick-setting anhydrite, $CaSO_4$, and the ordinary, or slow-setting, anhydrite, there is a second dihydrate, which is rhombic, and probably a slow-setting semihydrate. When gypsum is dehydrated by heating in a current of air at 98—130°, the rate of dehydration is less at the beginning, as had already been observed, and Davis states that this is due to a transformation taking place from the monoclinic to the rhombic dihydrate, which is the substance which really is dehydrated, and not gypsum itself. It is also this variety which is formed, in the first instance, when either the semihydrate or soluble anhydrite sets; afterwards, it slowly transforms into gypsum. In view of the new facts, much of the work on this subject by van't Hoff and his pupils would appear to be rendered of doubtful value.

A peculiar effect of potassium dichromate in retarding the rate of dissolution of magnesium in acetic acid is noted by Lohnstein[58]; if the concentration of dichromate is increased beyond a certain point, action stops altogether, and the concentration necessary to effect this increases with increasing concentration of the acid; after inhibition in this way, dissolution will re-commence, however, if the magnesium is made the anode of an electrolytic cell arrangement. The alkali salts and magnesium salts of strong acids destroy the passivity.

A new method of preparing crystallised magnesium oxide is described by Houdard[59]; it depends on the use of fused magnesium sulphide as a solvent. The two substances are heated together in an electric furnace, and the crucible is allowed to cool slowly; the sulphide can be dissolved away with acid, leaving cubic, optically isotropic crystals of oxide. These dissolve only slowly in warm hydrochloric or nitric acid, more rapidly in sulphuric acid.

An interesting amino-compound, corresponding with potassium zincate, is described by Fitzgerald[60] and by Franklin.[61] It is best obtained, as well-formed crystals, by acting with excess of potassamide in anhydrous ammoniacal solution on the compound of zinc iodide and ammonia. Its composition is represented by the formula $(KNH)_2Zn,2NH_3$; in absence of ammoniacal salts, it is sparingly soluble in ammonia; it is rapidly acted on by water or dilute acids. When heated in a vacuum it is stable as far as 160° at least, loses a good deal of ammonia at 260°, and is more profoundly changed at higher temperatures.

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[57] *Abstr.*, 1907, ii, 686.
[58] *Ibid.*, 769.
[59] *Ibid.*, 621.
[60] *Ibid.*, 545.
[61] *Ibid.*, 768.

A peroxide of mercury was obtained by Bredig and Antropoff[62] as a brown solid by the action of 30 per cent. hydrogen peroxide on mercury at low temperatures, and in presence of traces of acid. The compound has been further investigated by Pellini,[63] who obtained it as above, and also by the interaction of hydrogen peroxide and mercuric chloride and the equivalent quantity of potassium hydroxide, all in alcoholic solution; when prepared by the latter method, it is less stable, rapidly decomposing with formation of mercuric oxide. It is a brick-red powder, which shows no indications of crystalline character. It is decomposed slowly by water, giving basic oxide, oxygen, and hydrogen peroxide; with acids generally, it gives mercuric salt and hydrogen peroxide, but with hydrochloric acid chlorine is formed; with potassium iodide, iodine is liberated; potassium permanganate is decolorised. Unlike lead dioxide, therefore, it is a true peroxide.

Vicario[64] points out that considerable discrepancies exist in the data regarding the solubility of mercuric bromide, and shows that this is due to hydrolytic decomposition of the salt, which is very decided on heating; oxybromides are formed, and may be obtained as crystallised, yellow solids. A double salt, $2NaBr,HgBr_2$, is formed when sodium bromide is added along with the mercuric bromide, and a similar mixed compound is also formed by sodium chloride; these are very soluble, and their solutions are not decomposed by boiling.

Group III.

Concerning boron, there is very little to report. The various crystalline calcium borates formed from solution have been studied by Meyerhofer and van't Hoff[65] for the purpose of reproducing artificially certain of the complex borates found in nature; some of these were obtained, but the salts are of slight general interest. In the case of the lithium borates examined by Dukelski[66] in continuation of his work on the potassium and sodium salts referred to in the last Report, three distinct borates appear to be formed at 30°; of these, the monoborate, $Li_2O,BrO_3,16H_2O$, and the pentaborate, $Li_2O,5BrO_3,10H_2O$, crystallise, but the diborate, which would be the analogue of borax, was obtained only in an amorphous form, in which the amount of water could not be accurately determined.

Regarding aluminium, it may be noted that a fair amount of work is recorded on the use of aluminium itself as a reducing agent for the preparation of metals, alloys, &c. The behaviour of nitric acid and aluminium has been studied by van Deventer[67]; the action of dilute acid is slow, and is proportional to metal surface and to concentration of acid; chemically, it is quite different from the action with zinc, since there is little or no formation of ammonia, although there is some liberation of nitrogen; the greatly predominating action is that expressed by the equation: $Al + 4HNO_3 = Al(NO_3)_3 + 2H_2O + NO$.

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[62] *Zeitsch. Elektrochem.*, 1906, **12**, 585.

[63] *Abstr.*, 1907, ii, 954.

[64] *Ibid.*, 772.

[65] *Ibid.*, 542.

[66] *Ibid.*, 542.

Houdard[68] has succeeded in preparing a series of sulphur derivatives of aluminium, analogous to the spinels; three of these, which have been isolated more or less pure and well crystallised, belong to the cubic system, as the spinels themselves do; these three have the composition $Mn(AlS_2)_2$, $Fe(AlS_2)_2$, and $Cr(AlS_2)_2$ respectively. The compounds are obtained by heating in a current of hydrogen sulphide a mixture of aluminium turnings and the appropriate metal, or its sulphide, contained in a carbon boat; the temperature employed is at first a red-heat, but later a white-heat. The resulting mass is treated with water, acetic acid, &c.

During the past year, there has been a fair amount of work dealing with the chemistry of thallium. As regards the relation of thallous compounds to those of the alkali metals and of ammonium, Tutton[69] has made an interesting comparison of sulphates and selenates in extension of his well-known work on this isomorphous group. Whilst the thallous compounds are rhombic and isomorphous with the others, they do not show the same regular relationship regarding variation of crystal properties with variation in atomic weight of the metal; thallium is therefore not a member of what, it is suggested, might be called the "eutropic" series containing potassium, rubidium, and cæsium.

O. Rabe[70] has further investigated the thallic oxide prepared by him, as mentioned in last year's Report. When heated, this oxide is much more stable than is generally supposed; it remains undecomposed, but is slightly volatile, at 600°, melts at about 720°, and decomposes rapidly above 800°, forming thallous oxide and oxygen.

The compounds of thallium with the sulphur group of elements have been investigated by Pélabon[71] by means of fusion mixtures. The lowest sulphide thus formed is Tl_2S, which floats as a separate layer on any excess of metal present; at the other end of the scale, two layers are also formed, one of sulphur, and the other of pentasulphide, Tl_2S_5; at intermediate stages, there is separation of Tl_8S_7. With selenium and tellurium, similar end-members of the series are observed, but the intermediate stages are different. The formation of thallium sulphides in the wet way has been studied, along with other matters relating to the chemistry of thallium, by Hawley.[72] He treated thallous sulphide with sodium sulphide solutions containing extra sulphur, and then saturated with hydrogen sulphide. He concludes that the highest sulphide thus formed is Tl_2S_3, and that this forms a complete series of solid solutions with Tl_2S. He has also studied the products obtained by the simultaneous precipitation with hydrogen sulphide of solutions of thallous salts mixed with compounds of arsenic and antimony, and finds that thallous sulphide forms more or less complete series of solid solutions with arsenious sulphide, antimonious sulphide, and antimonic sulphide. With arsenic sulphide, it forms a definite thioarsenate, Tl_2AsS_4, but no solid solutions. For the determination of thallium, Hawley proposes the use of sodium thiostannate as precipitated, since the thallous salt, Tl_4SnS_4, is practically insoluble in water, and can be dried on a Gooch filter at 105° without change.

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[67] *Abstr.*, 1907, ii, 265.
[68] *Ibid.*, 468, 550.
[69] *Ibid.*, 688.
[70] *Ibid.*, 769.
[71] *Ibid.*, 770.

A very full and complete statement regarding the halogen compounds of thallium, the result of researches published from time to time in preceding years, is given by V. Thomas,[73] and particulars are given regarding various thallous salts by Stortenbeker.[74]

Group IV.

When Moissan succeeded in preparing artificial diamonds by the process of suddenly chilling the outer portion of a quantity of liquid iron saturated with carbon and then allowing the core to solidify gradually, it was supposed that the reason for some of the carbon crystallising in an exceptional manner was to be found in the very high internal pressure developed during the second part of the operation. This explanation is rendered doubtful, however, by the results of experiments conducted by C. A. Parsons.[75] Cores of carbon, or of carbon and iron, suitably enveloped, were subjected to the action of exceedingly strong electric currents with simultaneous application of direct pressure, which, in some instances, rose as high as 100 tons to the sq. inch; soft graphite was the usual form in which the carbon was found on cooling, and in no instance was there any distinct indication of the formation of diamond, although the pressures employed were probably higher than those obtainable in Moissan's process. The latter's views are also criticised by van Deventer[76] from the theoretical standpoint.

An interesting study regarding the direct union of carbon and nitrogen, and the decomposition of cyanogen, has been made by M. Berthelot.[77] From his results, it appears that carbon and nitrogen, if both are perfectly pure, show no tendency to unite when heated with each other, even up to the temperature of the electric arc. Previous results, which have seemed to indicate the contrary, were doubtless obtained with impure materials, especially with impure carbon, since it is exceedingly difficult to prepare this element pure, and therefore it is advisable that natural diamond should be used. The most important impurities are, in the first place, hydrogen compounds, which give rise to the production of acetylene, and so of hydrocyanic acid; in the second place, metallic compounds, which give rise to cyanides. If pure carbon and nitrogen could unite, equilibrium should be attained in the direct decomposition of cyanogen, but when this gas is submitted to the action of powerful electric sparks it is apparently completely decomposed; the solid deposited is a mixture of polymerisation products and carbon, and the residual gas is pure nitrogen.

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[72] *Abstr.*, 1907, ii, 460, 770.

[73] *Ibid.*, 547.

[74] *Ibid.*, 770.

[75] *Ibid.*, 762.

[76] *Ibid.*, 456.

Two new metal-carbonyl compounds have been described. From the compound $Fe_2(CO)_9$ (which, as stated in the Report for 1905, is formed on exposure of $Fe(CO)_5$ to bright sunlight), Dewar and H. O. Jones[78] have obtained the tetracarbonyl, $Fe(CO)_4$. When the first-mentioned compound is heated with various liquids in an atmosphere of carbon dioxide to a temperature of 50—90°, intensely green solutions are formed; from the solution thus formed with toluene, green crystals of the new compound can be obtained. If the solid is heated alone or in solution, it decomposes at or below 140° with deposition of iron and liberation of carbon monoxide. Its molecular weight appears to be very high, from the very slight depression of the freezing point which it brings about in benzene solution.

The second new carbonyl compound, or, rather, a derivative of it, was obtained by von Bartal[79] in the course of an investigation of the action of carbonyl chloride on the aluminium halides. When aluminium iodide is fused at about 200° and treated with the vapour of carbonyl chloride until it has gained in weight to the extent of 25 per cent., the solid product which forms on cooling gives up iodine and unchanged iodide when repeatedly digested with carbon disulphide, and leaves a brown, amorphous powder; the composition of this corresponds with the formula $Al_3(CO)_2Cl_2I$. The solid decomposes when heated to about 300°, losing aluminium halides, and leaving a black residue containing aluminium and carbon, but no halogen. From the general behaviour of the substance, von Bartal concludes that the original substance consists of a double compound, $Al_2(CO)_2,AlCl_2I$. One of the products of the action of carbonyl chloride on aluminium bromide is carbonyl chlorobromide, COClBr, which von Bartal obtained pure as a practically colourless liquid of disagreeable odour, and boiling at 25°.

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[77] *Abstr.*, 1907, ii, 257.
[78] *Ibid.*, 266.
[79] *Ibid.*, 957.

The reduction of carbon dioxide to formaldehyde has been effected by Fenton[80] by passing a rapid stream of the gas through pure water in which rods of amalgamated magnesium are immersed. The amount of aldehyde formed is small, but the proportion is increased in presence of certain substances, such as ammonia or phenylhydrazine.

A number of complex carbonates, including acid salts, have been prepared by various workers. T. B. Wood and H. O. Jones[81] have obtained potassium cupric carbonates (previously described by Reynolds) by the action of a mixed solution of potassium carbonate and bicarbonate on basic cupric carbonate. From the behaviour of this salt (and also of potassium cobaltous carbonate) on electrolysis, the authors conclude that these double carbonates give in each case a complex ion, $M(CO_3)_2''$, in solution. Raikow[82] has investigated the formation of carbonates by the action of carbon dioxide on suspensions of bases in water. (In some cases, the suspensions were obtained by treating a normal solution of a salt of the metal with one-fifth of the equivalent of alkali, and they would therefore contain basic salts and not hydroxides.) In the great majority of cases, the quantity of carbon dioxide taken up corresponded with the formation of normal salt, but in some cases only basic salts could be found, whilst in others acid salts were obtained; two unstable compounds belonging to a new type of acid carbonate were produced, $Ni_3H_2(CO_3)_4$ and $Cu_3H(CO_3)_2$, from nickelous and cuprous hydroxides respectively.

In order to prepare crystallised silicon free from the small quantities of iron with which it is found always to be associated when obtained by heating potassium fluosilicate with aluminium in a clay crucible, Vigouroux[83] recommends that the impure material be finely powdered and digested for some hours with diluted hydrofluoric acid, then washed, and heated with concentrated sulphuric acid; this process of purification is to be repeated until a sample yields no residue when heated with a mixture of nitric and hydrofluoric acids. All operations are conducted in platinum vessels.

Methods for the preparation of pure titanium tetrachloride are given by Vigouroux and Arrivaut[84] and by Ellis.[85] The former start from commercial ferrotitanium, either using it directly or, preferably, first removing the greater part of the iron by means of hydrochloric acid. The material is heated in a porcelain tube, and a current of dry chlorine is passed over it, which causes incandescence. Most of the ferric chloride which is formed condenses in the cooler part of the tube (which must be wide to prevent choking), and the titanium compound is condensed by means of air and water condensers; the filtered liquid is then fractionated. Ellis starts with rutile, which is first powdered (this is easily effected if the mineral is strongly heated and then chilled), then dried, mixed with aluminium, and the mixture ignited by means of a magnesium fuse. The resulting material is transferred to a combustion tube, and treated with dry chlorine. The condensed product is condensed and fractionated; chlorine and silicon chloride first pass over; the amount of the latter may be considerable, depending on the amount of silica and silicate present with the rutile.

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[80] *Trans.*, 1907, **91**, 687.

[81] *Abstr.*, 1907, ii, 621.

[82] *Ibid.*, 170, 171.

[83] *Ibid.*, 82.

[84] *Ibid.*, 97, 270.

[85] *Ibid.*, 270.

The question as to the nature of "pertitanic acid" is discussed by Faber[86]; he finds that its solutions behave so much like solutions of hydrogen peroxide that the existence of sexavalent titanium compounds might be considered dubious. He has, however, succeeded in preparing two new yellow compounds which he believes give conclusive evidence of such existence. One is an acetate derivative, which is so explosive that it could not be properly analysed; the other is a phosphate which corresponds with the formula $Ti(OH)_3PO_4$. The author assumes that the titanium has become sexavalent by the direct addition of two hydroxyl groups; in that case, the compound should not regenerate hydrogen peroxide when decomposed, but on this point he gives no information.

The investigation of zirconium salts by A. Rosenheim and others[87] is continued. As a rule, it is found that basic compounds, salts of the radicles (ZrO) and (Zr_2O_3), are obtained by crystallisation from solutions in acids; a considerable number of such salts, simple and double, and derived both from organic and inorganic acids, are described (chlorides, nitrates, sulphates, oxalates, tartrates). In circumstances where hydrolysis cannot occur, however, and also in some special cases even when water is present, normal derivatives are obtainable. For example, when zirconium tetrachloride is heated with formic, acetic, or propionic acid, the whole of the chlorine is evolved as hydrogen chloride, and normal formate, acetate, or propionate is formed. The normal acetate undergoes gradual hydrolysis when exposed to air which is dried by sulphuric acid, forming zirconyl acetate; in ordinary air, this acetate undergoes complete hydrolysis. Zirconium chloride reacts with many organic compounds, for example, with many esters, to form either direct additive products or derivatives in which half of the chlorine is replaced by organic groups; thus, salicylaldehyde yields the compound $ZrCl_2(O\cdot C_6H_4\cdot COH)_2$. The authors find that many of the published data regarding the basic zirconium salts are erroneous; this is confirmed also by Arthur Müller[88] from his experience in preparing colloidal zirconium hydroxide from the nitrate.

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[86] *Abstr.*, 1907, ii, 557.

[87] *Ibid.*, 271.

Bellucci and Parravano[89] have prepared hydrosols of plumbic acid (hydrated peroxide) by dialysis from potassium plumbate; the ratio $K_2O : PbO_2$ may be reduced thus to 1·87 : 98·13. The liquid may be taken to a syrupy consistency on the water-bath without coagulation, and the hydrosol is fairly stable. When added to pure water, it causes no appreciable lowering of the freezing point. The subject has also been studied by Parravano and G. Calcagni.

The well-known changes which take place on heating the products of the partial oxidation of lead sulphide, and which play such an important part in the metallurgy of lead, have been very fully studied by Schenck and Rassbach,[90] who show that the process is more complex than has generally been assumed. This is due to the fact that reversible actions are involved, and from the investigation of the equilibrium conditions the authors conclude that the following four equations represent the chemical reactions which actually occur:

$$PbS + PbSO_4 \rightleftharpoons 2Pb + 2SO_2; \quad PbS + 2PbO \rightleftharpoons 3Pb + SO_2;$$
$$PbS + 3PbSO_4 \rightleftharpoons 4PbO + 4SO_2; \quad Pb + PbSO_4 \rightleftharpoons 2PbO + SO_2.$$

Only one compound of lead and selenium, namely, PbSe, can be obtained by fusing together the two elements, although, when excess of selenium is used, the lower of the two layers formed contains nearly twice as much selenium as corresponds with the monoselenide. This is shown by Pélabon[91] to be due merely to the solubility of the selenium in the fused monoselenide; the upper layer is practically pure selenium.

Descriptions of thorium compounds are given by Matignon and Delépine,[92] the principal being the tetrachloride and oxychloride, the nitride (Th_3N_4), and the hydride (ThH_4).

Group V.

The synthetic production of ammonia under the influence of electric sparks has been studied by Briner and E. Mettler.[93] For their experiments they prepared the gaseous mixture of the elements by passing dry ammonia over electrically heated spirals of nickel, platinum, or iron, and subsequent treatment with sulphuric acid. The proportion of ammonia formed, which amounts to only 3—4 per cent. at the ordinary temperature, increases with falling temperature, and the action is nearly complete at the temperature of liquid air. The influence of pressure was also studied, and found to be peculiar, since, within the working range of 20—800 mm., there was found to be (at 100 mm.) a marked maximum in the efficiency with regard to the energy expended; the production at this pressure was 0·17 gram of ammonia per kilowatt hour.

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[88] *Abstr.*, 1907, ii, 272.
[89] *Ibid.*, 86, 87.
[90] *Ibid.*, 546, 619.
[91] *Ibid.*, 547.
[92] *Ibid.*, 179.
[93] *Ibid.*, 342.

Another method for the synthetic production of ammonia forms the subject of a patent by Kaiser.[94] His process depends on the alternation of the action of hydrogen on calcium nitride, which yields ammonia and calcium hydride, with that of nitrogen on calcium hydride, which also yields ammonia and regenerates calcium nitride; it is advisable that the solid material should be finely divided and expose a large surface. The most suitable temperature is between 200° and 400°, although the reaction sets in about 150°.

In the case of the elements magnesium, titanium, boron, cerium, molybdenum, and tungsten, either a nitride cannot be formed by direct union or else the nitride does not yield ammonia with hydrogen. Cerium nitride does yield hydride and ammonia, and the nitride can be regenerated by nitrogen, but the gases require to be purer than is practicable for a technical process.

There has been considerable discussion recently as to the formation of a definite ammonium amalgam, and the general tendency is apparently in favour of its existence.

The investigation of hydrazoic acid (azoimide) and some of its derivatives has been continued by L. M. Dennis and Miss Isham.[95] The pure acid was prepared by the distillation of small quantities of the potassium compound with somewhat diluted sulphuric acid, the vapours, after drying, being condensed by means of liquid air; the product thus obtained was proved by analysis to contain 99·94 per cent. of the acid. The boiling point given by Curtius, 30°, was confirmed, and the freezing point was found to be −80°. The vapour density was determined by Victor Meyer's method, and found to agree with the simple formula, HN_3. The greatest care had to be exercised in working with the acid, and considerable use of liquid air had to be resorted to, so as to freeze it and thus facilitate its manipulation. For example, in the first attempts to determine the vapour density (before freezing was resorted to) the material always exploded violently when the containing bulb was broken, and even with so small a quantity as 0·011 gram both vessels of the apparatus were completely shattered. The copper and zinc salts form compounds with ammonia and with pyridine, $CuN_6,2NH_3$, &c.; the cobalt and nickel salts unite with pyridine in higher proportions. In connexion with the quantitative determination of azoimide, it is pointed out that when treated by Kjeldahl's method it yields one-third of its nitrogen as ammonia. A. W. Browne and Shetterly[96] show that azoimide may be formed in appreciable quantity during the oxidation of hydrazine, for example, by the action of ammonium metavanadate.

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[94] *Abstr.*, 1907, ii, 862.

[95] *Ibid*, 165, 255.

H. B. Baker and Mrs. Baker[97] have made the interesting discovery that nitrogen trioxide can be obtained in the gaseous form by volatilisation of the liquid into an atmosphere of nitrogen which has been dried as completely as possible, so that apparently the dissociation into nitrogen peroxide and nitric oxide (like that of ammonium chloride, &c.) takes place only in presence of moisture. The evidence is provided by vapour density determinations according to Victor Meyer's method; these, under the special conditions indicated, gave numbers varying from 38 to 62, and, since the theoretical number for N_2O_3 is 38, it is therefore to be presumed that polymerisation takes place with formation of N_4O_6 molecules.

According to Manchot and Zechentmayer,[98] and G. von Hüfner,[99] it appears that the absorption of nitric oxide by solutions of ferrous salts (and also of nickelous, cobaltous, and manganous salts) takes place to an extent such that the ratio $NO:Fe^{\cdot\cdot}$ approaches, but does not exceed unity, provided due allowance is made for the absorption due to the water itself. Apparently, therefore, there is some sort of compound formed; the union is so slight, however, that the ordinary absorption laws hold. According to Kohlschütter and M. Kutscheroff,[1] the absorption by ferrous chloride is nearly doubled if solution in 30 per cent. hydrochloric acid is used in place of aqueous solution, although the effect is diminished rather than increased if 10 per cent. acid is used.

Two papers by Böeseken[2] deal with the properties of pure ordinary phosphorus, and the change of the latter into the red modification. According to him, the pure substance is perfectly white, and remains so if kept in the dark in evacuated tubes, but it soon becomes yellow on exposure to light; the common yellow phosphorus, which has been melted under water, always retains a considerable quantity of moisture, and has lower density and a lower melting point than the pure substance. To obtain the latter, he heats phosphorus with chromic acid solution, washes, dries in a vacuum, first at 40°, then at 80°, and lastly distils. Böeseken finds that in evacuated tubes aluminium chloride brings about the change to red phosphorus below 100°, especially if phosphorus trichloride is present to act as solvent. To explain such catalytic changes, he holds that it is necessary to assume that the transformation is preceded by a breaking up of the P_4 molecule, and that the products of this dissociation (P_2 or P) thereupon polymerise to form the more complex molecule of the red variety; the dissociation is a very slow action, and it is this which is accelerated by the various catalytic agents. To demonstrate this change experimentally, Zecchini[3] heats from 10 c.c. of dried phosphorus in a glass tube immersed in a bath of sulphuric acid at 180°, and then drops in a small crystal of iodine, whereupon practically the whole of the phosphorus undergoes transformation.

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[96] *Abstr.*, 1907, ii, 863.
[97] *Trans.*, 1907, **91**, 1862.
[98] *Abstr.*, 1907, ii, 93.
[99] *Ibid.*, 552.
[1] *Ibid.*, 267.
[2] *Ibid*, 343, 760.

According to Jungfleisch,[4] pure oxygen at atmospheric pressure oxidises dry phosphorus directly to phosphoric oxide only; but, if the concentration is very considerably diminished by lowering the pressure or mixing with inert gas, then phosphorous oxide also is formed, along with a yellow lower oxide, P_4O. The process can be so regulated as to produce crystals of phosphorous oxide. This is exceedingly inflammable, and, on admission of air or oxygen, takes fire before any phosphorus which may be present.

An interesting method of completely decomposing phosphates, and volatilising all the phosphorus compounds formed, is described by Jannasch and Jilke.[5] It consists in heating the substance in a stream of chlorine laden with vapour of carbon tetrachloride. The experimental work so far completed deals only with ammonium and magnesium phosphates; with them the process of volatilisation is complete in the course of several hours.

In connexion with an investigation of the changes which take place on the heating of ammonium salts, Dehn and Heuse[6] find that the phosphates and arsenates give off water and ammonia simultaneously from the first, and that the residues obtained as intermediate products are of indefinite composition. On this account it appears highly probable that many so-called compounds which are stated to have been prepared in this way are really complex mixtures.

Hewitt and Winmill[7] find, from the results obtained by the ebullioscopic method with solution in carbon disulphide, that arsenic di-iodide has the composition As_2I_4. As stated by Bamberger and Phillip, who first prepared it, the decomposition by water ($3As_2I_4 = 4AsI_3 + 2As$) is not complete; a complete decomposition in this sense takes place, however, when the compound is treated with pyridine.

Apparently ortho-arsenic acid does not exist as a solid having the composition H_3AsO_4; according to Baud,[8] the highest solid hydrate derived from the pentoxide, namely, $4H_2O,As_2O_5$ (presumably H_3AsO_4,H_2O), effloresces to form pyro-arsenic acid, $H_4As_2O_7$, directly, no intermediate compound being obtainable.

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[3] *Abstr.*, 1907, ii, 681.
[4] *Ibid.*, 761.
[5] *Ibid.*, 864.
[6] *Ibid.*, 766.
[7] *Trans.*, 1907, **91**, 962.
[8] *Abstr.*, 1907, ii, 761.

The method of preparing antimony pentafluoride, by the action of hydrofluoric acid on the chloride, has been improved, and the substance itself investigated, by Ruff and others.[9] It forms a number of interesting additive products. With chlorine it does not unite; with bromine it yields a mass which possibly contains the compound SbF_5Br; with iodine it forms two compounds, $(SbF_5)_2I$ and SbF_5I. It dissolves sulphur with formation of a blue solution, from which the compound SbF_5S can be isolated. With a small quantity of water it unites to form the solid hydrate $SbF_5,2H_2O$, which is soluble in water; the solution is not very readily acted on by reagents such as hydrogen sulphide, potassium iodide, &c.

Well-defined, crystalline double sulphates of antimony and the metals of the alkaline earths, and silver, have been prepared by Kühl[10] from solutions of the constituent salts in concentrated sulphuric acid. Those with metals of the alkaline earths have the composition $MSb_2(SO_4)_4,6H_2O$; the silver salt is similar, but anhydrous. They are all decomposed by water.

There has been a fairly considerable amount of new work dealing with vanadium. The preparation and properties of the element itself, and also of columbium and tantalum, are described by W. Muthmann, L. Weiss, and R. Riedelbauch[11]; the method of preparation used is a modified "thermite" process, in which a "mixed metal" obtained from the rare earths is employed in place of aluminium. A considerable amount of information regarding columbium and its properties is also given by W. von Bolton,[12] who prepared the pure element by reducing the pentoxide with aluminium, and volatilising the excess of aluminium, and other impurities, by heating electrically in a vacuum for several hours. The values given for some of the physical properties differ considerably from those of the preceding authors.

The preparation of pure hypovanadic acid, and of a considerable number of compounds derived from it, is described by Gain.[13] His starting point is the mixture of oxides (V_2O_3 and V_2O_4) left when ammonium metavanadate is calcined; this is treated with saturated sulphurous acid solution, and a blue solution is thus obtained, from which the compound $2V_2O_4,3SO_2,10H_2O$ can be crystallised. This loses sulphurous acid when boiled with water, and hypovanadic acid, $H_4V_2O_5$, is deposited as a pale reddish crystalline powder. From this, and from the blue solution, a series of blue crystalline vanadyl sulphates can be obtained by the action of sulphuric acid. Compounds more or less similar to these are also obtainable from selenic, orthophosphoric, and ortho-arsenic acids. The blue solution also yields a series of double sulphites when it is mixed with solutions of the acid sulphites of ammonium, thallium, and the alkali metals, and then evaporated at a low temperature. Mawrow,[14] by acting on vanadic acid with hypophosphorous acid, has prepared a di-vanadyl hypophosphite, $V_2O_2(H_2PO_2)_2,2H_2O$, from which, by the action of alkali, di-hypovanadates are obtained, for example, the ammonium salt, $(NH_4)_2V_4O_9,3H_2O$.

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[9] *Abstr.*, 1907, ii, 98.

[10] *Ibid.*, 627.

[11] *Ibid.*, 781.

[12] *Ibid.*, 478.

[13] *Ibid.*, 32, 97, 558, 627.

Group VI.

F. Fischer and Hans Marx,[15] in continuation of work referred to in last year's Report, give further particulars regarding the production of ozone and hydrogen peroxide when air or oxygen is blown over a glowing Nernst-filament; the yield of ozone increases with rise of temperature of the filament, but falls with rise of temperature of the gas current; the shape of jet used also influences the yield. For air, the maximum yield was 0·13 per cent. of the oxygen present; with oxygen a better yield is obtained by using a slow current. When moist gas is used, the yield of ozone diminishes considerably, but hydrogen peroxide is then formed also. If a glowing filament is plunged into liquid oxygen, the yield of ozone depends on the duration of the experiment; as much as 3·91 per cent. was obtained after ten hours.

Some interesting results regarding the preparation of ozone electrolytically are given by F. Fischer and Massenez.[16] By suitable arrangements of the apparatus and conditions employed, they have succeeded in obtaining products containing as much as 28 per cent. of ozone by weight. Various types of anode were tried; that which gave the best result was formed from a platinum tube coated with glass, with a narrow slit cut through this coating so as to expose a very small surface of platinum. The anode was kept cold by a current of calcium chloride solution cooled to −14°, whilst the electrolyte itself was kept at 0°. The most suitable electrolyte is sulphuric acid of concentration such that the layer of greater concentration formed at the anode becomes acid of maximum conductivity. The surface of the anode should be kept as smooth as possible.

According to E. Merck,[17] a good yield of hydrogen peroxide can be obtained from barium peroxide, suspended in water, by the action of carbonic acid, provided the barium peroxide is kept in excess; with excess of carbonic acid, very little hydrogen peroxide is obtained owing to the formation of fairly stable barium percarbonate, $BaCO_4$. This salt, prepared at low temperature from either hydrated or anhydrous peroxide, can be used for the preparation of hydrogen peroxide, by treating it with the appropriate quantity of an acid which forms an insoluble barium salt.

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[14] *Abstr.*, 1907, ii, 782.
[15] *Ibid.*, 163, 340.
[16] *Ibid.*, 162, 254.
[17] *Ibid.*, 859.

From a study by A. Fischer[18] of solutions prepared from pure hydrogen peroxide, it appears that very slight concentrations of sulphuric and hydrochloric acids are highly efficient in retarding decomposition; phosphoric acid is less effective, and boric acid still less so; oxalic acid, so far from decomposing the peroxide, is, in concentrations of 0·1—2 per cent., a more efficient preservative than either hydrochloric or sulphuric acid.

The peculiarities exhibited by molten sulphur, and the differences observed in different varieties of precipitated sulphur, now seem to be satisfactorily explained, as a result of the investigations by A. Smith and his collaborators.[19] The conclusions arrived at are that when sulphur is fused, two modifications result, which are distinguished as S_λ and S_μ and these are dynamic isomerides.[20] S_λ is comparatively mobile, and is light in colour; S_μ is viscous and dark. The proportion of S_μ is small at low temperatures, but increases with rising temperature; if the temperature is raised rapidly, there may be a decided lag, so that some time may elapse before equilibrium is established. The rate of transformation can be greatly retarded by certain agents, such as sulphur dioxide or hydrochloric acid, but this effect can be reversed by others, such as ammonia. Advantage is taken of this in determining the state of equilibrium at any given temperature; equilibrium is established rapidly with the help of ammonia, then a retarding gas is passed in, and the liquid sulphur is rapidly chilled in water. The solid obtained from S_λ is crystalline, and soluble in carbon disulphide, whilst that from S_μ is amorphous and insoluble. When ordinary sulphur is heated, there is always considerable retardation, owing to the invariable presence of sulphur dioxide in sulphur which has been exposed to air. (According to Moissan,[21] even sulphur which has been melted and cooled in a vacuum cannot be obtained free from bubbles of hydrogen sulphide and sulphur dioxide when it is remelted; these gases are formed from traces of water which it is almost impossible to remove.)

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[18] *Abstr.*, 1907, ii, 161.

[19] *Ibid.*, 20, 451, 757.

[20] F. Hoffmann and R. Rothe (*Abstr.*, 1907, ii, 539) claim that in this matter their views have been adopted by Smith and his colleagues without acknowledgment; but this charge is satisfactorily rebutted by the latter (*Zeitsch. physikal. Chem.*, 1907, **61**, 207).

[21] *Abstr.*, 1907, ii, 341.

The amount of S_μ present in liquid sulphur at 114·5°, at which temperature it is in equilibrium with solid S_β, is only 3·7 per cent.

As regards precipitated sulphur, the conclusions drawn are that the sulphur separates first in liquid form as S_μ, which, however, changes more or less rapidly to S_λ, and ultimately to S_α. The rate of transformation varies greatly with the nature of the liquid in contact with the liberated sulphur. The soluble varieties of precipitated sulphur are merely S_α; the insoluble varieties are those in which solidification has taken place before any great proportion of S_μ has been transformed into S_λ.

Paternò and Mazzucchelli[22] have investigated the blue variety of sulphur described by Orloff, and have also examined many cases of formation of blue colorations in which sulphur compounds are involved. They conclude that although there may be some cases in which the coloration is due to the presence of this variety of sulphur, as a rule there is no reason to assume that this is so; certainly there can be no free sulphur involved in the case of ultramarine, since the blue colour persists after the substance is heated to bright redness for some time.

For the preparation of hydrogen sulphide, Fonzes-Diacon[23] recommends the method of dropping water on solid aluminium sulphide; this is prepared by igniting, by means of a magnesium ribbon fuse, a mixture of sulphur and aluminium in a crucible.

The synthesis, and the dissociation, of hydrogen sulphide have been the subject of investigation by Milbauer[24] and Preuner.[25] The papers are chiefly of physico-chemical interest; but, with regard to the first-mentioned, it may be noted that the action is found to be accelerated by platinum black and by phosphorus, the effect in the latter case being due, presumably, to the actions: (*a*) $P_2S_5 + 8H_2 = 2PH_3 + 5H_2S$, (*b*) $2PH_3 + 4S_2 = P_2S_5 + 3H_2S$. Metallic sulphides appear to be without effect.

The properties of liquid hydrogen sulphide, and its character as a solvent, have been examined by Magri. Under atmospheric pressure it boils at −62° and freezes at −83°; its density is slightly less than that of water. It does not dissolve the salts of strong bases, but is a solvent for many of the compounds formed by non-metallic elements among themselves; some of these solutes increase the conductivity to some extent.

The precipitation of metallic sulphides from solutions of their salts, by means of hydrogen sulphide, forms the subject of several papers by Padoa and Cambi,[27] Bruner,[28] and Glixelli.[29] The first-named authors concern themselves chiefly with the pressure of hydrogen sulphide necessary for the precipitation of sulphide from acidified solutions, cadmium chloride, zinc sulphate, zinc chloride, and ferrous sulphate, and show that these pressures increase with increasing acidity. The two other authors named deal only with the precipitation of zinc sulphide, and their results corroborate each other. They find that the circumstances are complex; that the non-precipitation of zinc sulphide, from dilute acid solutions of ordinary zinc salts saturated with hydrogen sulphide, is due to a state of "false equilibrium," and not to the reversibility of the action (as is generally supposed), since the amount of zinc in solution is greatly in excess of what would be obtained by the action of such an acid solution on zinc sulphide; after a "period of induction," the duration of which increases with increasing acidity, precipitation sets in, and proceeds at a rate which also depends on the acidity. There are apparently two modifications of zinc sulphide, which differ greatly as regards solubility; for example, the sulphide precipitated from alkaline solution is nearly fifty times more soluble than that precipitated from acid solution. The above results indicate that in this matter zinc is quite analogous to cobalt and nickel, only in these cases the period of induction is much longer.

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[22] *Abstr.*, 1907, ii, 451.

[23] *Ibid.*, 164.

[24] *Ibid.*, 163.

[25] *Ibid.*, 861.

[26] *Ibid.*, 453.

[27] *Ibid.*, 86.

[28] *Ibid.*, 349.

[29] *Ibid.*, 868.

The quantitative composition of the products of combustion of sulphur in air and in oxygen has been studied by Kastle and McHargue.[30] With air, the proportion of sulphur converted into sulphur trioxide rises as high as 7 per cent., but with oxygen it averages only about 2·7 per cent.; in neither case is the ratio appreciably affected by the presence of moisture. The authors assume that the higher yields with air are due to the formation of nitrogen oxides which act as carriers; but since, with mixtures which contain less nitrogen than air does, the yield is lower than with air, it would appear not unlikely that it is largely a question of lower temperature benefiting the yield of sulphur trioxide.

The chemistry of the lead-chamber process has been dealt with by Raschig,[31] Lunge and Berl,[32] and Inglis.[33]. The first three papers form a continuation of the discussion referred to in last year's Report, and need not be further referred to. Inglis's contribution is a further instalment of his investigation into the loss of nitre; he concludes that the loss is very largely in the form of nitric oxide and peroxide, loss in the form of nitrous oxide being less than 10 per cent., and that in the form of nitrogen itself doubtful.

The reduction of concentrated sulphuric acid by hydrogen gas is

[30] *Abstr.*, 1907, ii, 861.

[31] *Ibid.*, 455, 863.

[32] *Ibid.*, 863.

[33] *Ibid.*, 613.

an action which is sometimes unjustifiably ignored in some branches of work; it has been studied very fully by Milbauer.[34] He finds that pure acid is almost unaffected at the ordinary temperature, but that there is a distinct action at higher temperatures. The catalytic effect of numerous substances was examined at 174°; the action is accelerated by a considerable number, including sulphates which are soluble in the acid, and notably so by the metals of the platinum group; it is retarded by many substances which are insoluble in the acid. Many of the substances which were tried were found to undergo reduction themselves, but some are oxidised, the most noteworthy cases being ferrous sulphate and mercurous sulphate.

An extended investigation of the action of alkalis on solutions of the sulphates of metals of the iron group, &c., has been made by Pickering.[35] In only two of the cases examined (magnesium and manganous sulphates) was hydroxide precipitated directly; in all others a basic salt of definite composition was first precipitated, to be further acted on by continued addition of alkali, with formation of a more basic salt or of hydroxide.

The formation of sodium thiosulphate from sulphite and sulphur has been examined by Kremann and Hüttinger[36] to see if it would throw any light on the retarding effect of glycerol, glucose, &c., on the formation of sodium sulphate from sulphite and oxygen. Since the retarding agents named have no influence on the formation of thiosulphate, it is concluded that in the other case they exercise their effect on the oxygen and not on the sulphite.

Some interesting results with regard to the electrolytic formation of persulphuric acid and persulphates have been obtained by Erich Müller and Schellhaas.[37] They find that the yield of persulphuric acid is very injuriously affected by the presence of Caro's acid; this is formed from the other by hydrolysis ($H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$), and undergoes decomposition at the anode, presumably by the action of discharged hydroxylion: $H_2SO_5 + 2OH = H_2SO_4 + H_2O + O_2$. The authors show that this loss of efficiency can be greatly diminished (1) by raising the anode potential by addition of some such substance as hydrofluoric acid; (2) by immediately reducing the Caro's acid, using some reducing agent which does not act similarly on persulphuric acid, for example, sulphurous acid; (3) by removing the persulphuric acid almost completely in the form of a persulphate which is practically insoluble in the liquid, such as the ammonium salt in very acid solution. By means of the second method, a current efficiency of more than 90 per cent. may be attained.

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[34] *Abstr.*, 1907, ii, 252.

[35] *Trans.*, 1907, **91**, 1981, 1988.

[36] *Abstr.*, 1907, ii, 758.

[37] *Ibid.*, 539.

Much work dealing with complex derivatives of chromic oxide has been carried out by J. Olie, jun.,[38] A. Colson,[39] R. F. Weinland and T. Schumann,[40] P. Pfeiffer,[41] A. Werner and J. Dubsky,[42] and N. Bjerrum.[43] The papers of Olie deal with chromic chlorides, especially the hydrates of the green salt; the proportion of the total chlorine which is precipitated by silver nitrate has been investigated, and it is found that this is considerably affected by the presence of acids and salts. In presence of strong acids, little more than one-third can be precipitated; whilst in presence of a high concentration of neutral salts it is nearly all precipitated; this limit is approached still more closely if silver salts of weak acids are employed in place of silver nitrate. Colson's work deals chiefly with the complexes in green chromic sulphate solutions, and the relations of those to the violet sulphate; he divides the green salts into three classes, according as one-third, two-, or three-thirds of the sulphate radicle is "masked," that is, cannot be precipitated by means of barium chloride in cold solution. The completely masked variety can be obtained from the residue left on spontaneous evaporation of a solution which has been exposed to sunlight during several months; it is also contained in the solution obtained by reducing chromic acid by sulphurous acid at −4°. Some of the compounds described by Weinland and Schumann are partly chloride, partly sulphate, for example, the salt,

$$CrClSO_4,8H_2O.$$

With barium chloride, a solution of this salt yields all its SO_4 as barium sulphate, but with silver nitrate it does not give an immediate precipitate. Other complex compounds are derivable from the chloride by union with ammonium chloride or sulphate. The chlorides, chlorosulphates, and bromides also form the subject of the contributions by Bjerrum.

The papers by Pfeiffer and Werner deal with salts of various complex "aquo," "hydroxylo," and "ammine" chromic derivatives, and form part of the extended investigation of these complexes derived from various metallic elements.

Derivatives of quinquevalent chromium have recently been obtained. The first of these were organic compounds,[44] for example, the pyridine derivative obtained by acting on chromic acid with cold concentrated hydrochloric acid and adding pyridine. Now, however, purely inorganic derivatives have been prepared by R. F. Weinland and M. Fiederer[45]; they are of the type $MCl,CrOCl_3$, where M is K, Rb, Cs, or (NH_4), and they are crystalline and of a dark red colour. They are prepared by dissolving chromic anhydride in hydrochloric acid at $-20°$, adding a solution of the appropriate chloride, and again saturating with hydrogen chloride; they are decomposed by moisture. As proof of their exact nature, the isomorphism of the cæsium compound with the corresponding columbium derivative was directly determined, by the formation of homogeneous mixed crystals of the two substances.

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[38] *Abstr.*, 1907, ii, 176, 177, 355.

[39] *Ibid.*, 167, 267, 356, 474, 780.

[40] *Ibid.*, 623, 877.

[41] *Ibid.*, 694.

[42] *Ibid.*, 966.

[43] *Ibid.*, 554, 622, 623.

[44] *Ibid.*, 1906, i, 37.

[45] *Ibid.*, 1907, ii, 31.

Much of the recent literature dealing with chromic acid and its salts need not be referred to, as it is concerned chiefly with the description of isolated salts and double salts. There has been considerable discussion as to the state of matters existing in aqueous solutions of dichromates; on the whole, the fresh physico-chemical evidence adduced by various observers tends in the direction of supporting Ostwald's view that in solutions of chromic acid and of dichromates the cations are principally Cr_2O_7'', and are not mostly split up into CrO_4'' and CrO_3, as supposed by Abegg and Cox.

From a full and careful study of solutions of potassium chromates with excess of chromic acid or potassium hydroxide respectively, and of the solids in equilibrium with them, I. Koppel and R. Blumenthal[46] have shown that the four compounds, K_2CrO_4, $K_2Cr_2O_7$, $K_2Cr_3O_{10}$, and $K_2Cr_4O_{13}$, exist throughout the whole range of temperatures from 0 to 60°, and that there is no evidence of the existence of any other derivative within these limits of temperature.

The most interesting points to be noted with regard to uranium are two papers dealing with uranous salts. For the preparation of some of these, especially the sulphate $U(SO_4)_2,4H_2O$, J. Aloy and Auber[47] recommend the reduction of uranyl salts by means of sodium hyposulphite.

A considerable amount of work has recently been done dealing with complex salts containing molybdenum; R. F. Weinland and H. Kühl[48] describe a number of sulphate-molybdate salts, of which the simplest is represented by the empirical formula,

$$K_2O,SO_3,2MoO_3,2H_2O;$$

they are obtained by the action of excess of sulphuric acid on molybdates, or by the action of concentrated solutions of sulphates on molybdenum oxysulphate; they all crystallise, and all are decomposed by water. A large number of double or complex molybdates, derived from chromium, aluminium, or iron, on the one hand, and the alkali metals, alkaline-earth metals, &c., on the other, have been prepared and described by R. D. Hall.[49]

From the fact that molybdic acid, when added to solutions of optically active hydroxy-acids, causes a very marked change in the rotatory power, it has been concluded that complexes are formed by the interaction of these substances; additional evidence in support of this view is provided by E. Rimbach and C. Neizert,[50] who find that on mixing isohydric solutions of molybdic acid and these optically active acids, there is a very marked increase of conductivity beyond what would otherwise be expected; this increase may amount to as much as 300 per cent.

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[46] *Abstr.*, 1907, ii, 356.

[47] *Ibid.*, 557; compare also A. Colani, *ibid.*, 878.

[48] *Abstr.*, 1907, ii, 625.

[49] *Ibid.*, 555.

Ordinary ammonium molybdate, $(NH_4)_{10}Mo_{12}O_{41}$, has been subjected to a physico-chemical investigation, according to various methods, by J. Sand and F. Eisenlohr,[51] and from the results they decide that in aqueous solution the composition of the anion is $Mo_{12}O_{41}$, with a tenfold charge; further that, when the solution is treated with alkali, these ions yield the anion, Mo_6O_{22}, with an eightfold charge, as an intermediate stage before passing into the final one of MoO_4'', when sufficient alkali is added.

Fluorine derivatives of sexavalent tungsten and molybdenum are described by O. Ruff, F. Eisner, and W. Heller.[52] The molybdenum compounds have the composition, MoF_6, $MoOF_4$, and MoO_2F_2, and there are similar tungsten derivatives; an interesting point concerning the oxy-compounds, as well as the others, is the fact that they can be obtained by the action of anhydrous hydrogen fluoride, in excess, on the corresponding chlorine derivative.

Group VII.

From a study of the freezing-point and boiling-point curves obtained for mixtures of the halogens, Karsten[53] draws the following conclusions: In agreement with the statements of Lebeau,[54] there is no evidence whatever that chlorine and bromine unite to form any compound—gaseous, liquid, or solid; the "compounds" described by other observers are solutions and mixed crystals of the two elements, and of the mixed crystals there is a continuous series. The compound ICl exists, not only in the liquid state, but also in the state of vapour; at the temperature of 100°, it is very slightly dissociated. In conclusion, it is pointed out that chlorine and bromine have less mutual affinity than bromine and iodine. Similar conclusions are drawn by Roozeboom,[55] who also shows that the compounds IBr and ICl_3 are very feeble, ICl being very stable in comparison.

Investigations on the basicity of hydrofluoric acid are published by Kremann and Decolle,[56] and by Pellini and Pegoraro[57]; from conductivity determinations on various solutions of acid and salts, both sets of observers conclude that hydrofluoric acid is dibasic, in harmony with the formula H_2F_2, deduced by other observers from cryoscopic determinations on not too dilute solutions of the acid.

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[50] *Abstr.*, 1907, ii, 269.
[51] *Ibid.*, 178, 179.
[52] *Ibid.*, 268, 624.
[53] *Ibid.*, 447.
[54] *Ibid.*, 843.
[55] *Ibid.*, 80.
[56] *Ibid.*, 756.
[57] *Ibid.*, 860.

Bourion [58] proposes a general method for preparing anhydrous bromides of the metals, which consists in heating an oxide of the metal to a suitable temperature (in no case above red-heat), and passing over it a current of hydrogen bromide, into which sulphur chloride is volatilised; the bromides are thus obtained either in the fused state, or more or less crystalline. In the case of the rare earths it was found that, no matter what oxalate be employed, the bromide formed is that corresponding with the formula MBr_3.

It is known that the presence of soluble chromate greatly increases the current-efficiency in the electrolytic preparation of hypochlorites and chlorates, but, owing to the colour, the use of such compounds is inadmissible in preparing electrolytic "bleach." Betts and Sherry [59] have therefore studied the effect produced by the addition of a number of other substances, but, although they have been partly successful in improving the results, they have found no substance so serviceable as sodium chromate. They found, however, that the use of certain metals as cathodes heightened the efficiency, both in chlorate and in hypochlorite preparations; a magnesium cathode gives results comparable with those obtained by adding chromate, but there is a considerable loss of magnesium—about 1 part for every 50 of chlorate made. In preparing hypochlorite, it was found that, by using cells in series, with carbon electrodes in the first and magnesium afterwards, the magnesium loss could be kept down to 0·2 part per 100 of chlorine, obtaining a conversion of 35—50 per cent. of salt, with a current efficiency of 60 per cent.

The action of dry hydrogen chloride on manganous dioxide suspended in carbon tetrachloride has been investigated by W. B. Holmes.[60] A solid material is obtained, which consists of manganese tetrachloride and trichloride; when this is treated with anhydrous ether, the trichloride dissolves, forming an intensely violet-coloured solution, leaving a reddish-brown residue of tetrachloride. The trichloride itself is a black solid with a greenish tinge; treated with alcohol, it yields a wine-coloured solution, which apparently contains the tetrachloride; when its ethereal solution is shaken with much water, only half of the manganese is precipitated. The tetrachloride dissolves in absolute alcohol, and the solution slowly decomposes and becomes colourless; in contact with ether it gradually yields trichloride, which dissolves; when heated to 100°, it evolves chlorine, and leaves manganous chloride; when the alcoholic solution is diluted with water, the whole of the manganese is precipitated.

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[58] *Abstr.*, 1907, ii, 773.

[59] *Ibid.*, 449.

[60] *Ibid.*, 873.

Muir[61] has succeeded in obtaining permanganic acid in the form of very unstable, violet-black crystals, by evaporation of the solution obtained by the interaction of barium permanganate and sulphuric acid. It was impossible to prepare the substance in a pure state owing to decomposition, it being always mixed with brown or black decomposition products.

Group VIII.

A large number of papers deal with alloys containing members of this group, but few of these provide matters of general interest. The influence on the specific volume and the specific heat of iron, exerted by various additions of carbon and metals, has been very fully studied by W. Brown.[62] The specific volume is increased by a number of elements besides carbon, although in some cases this holds only for small additions, and the effect is reversed with increased amounts; in a number of cases, the specific volume diminishes from the beginning. Other papers, dealing with special cast irons and steels, and with other similar iron alloys of actual or possible technological importance, refer principally to materials obtained by admixture of boron, tantalum, chromium, molybdenum, tungsten, and nickel, and to the influence which some of these exert on the nature and amount of the carbon retained by the iron. The exact nature of the "slag," or non-metallic impurities contained in steel, is described by E. F. Law[63]; as a rule, this material consists of sulphides or silicates of iron or manganese, and oxide of iron. Manganous sulphide is formed preferentially to ferrous sulphide, which therefore rarely occurs unless the proportion of manganese in the steel is low; the presence of patches of sulphide is recognised by coating the metal with a gelatin emulsion of a lead or cadmium salt. The silicates of the metals are very brittle, and their presence has therefore an important bearing on the behaviour of the material during rolling. Oxides, if present, are disseminated through the metal as minute specks, and have an important influence in increasing the corrosiveness of steel, due to electrochemical action; the amount present can be determined by reduction in a current of hydrogen, using special precautions. An interesting point connected with the occurrence of manganous sulphide in steel is also noted by A. A. Baikoff,[64] who considers that substance to be a normal constituent of steels, although in small quantity; he points out that the small but well-formed octahedral crystals, sometimes found in cavities in ingots, consist really of manganous sulphide, coated first with ferrite and subsequently with pearlite; they are therefore "epimorphs," the shape being derived from the kernel of sulphide.

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[61] *Trans.*, 1907, **91**, 1485.

[62] *Abstr.*, 1907, ii, 958.

[63] *Ibid.*, 692.

[64] *Ibid*, 874.

In connexion with the reinvestigation of the conditions of equilibrium in the system: Fe, FeO, C, CO, and CO_2, R. Schenck and others[65] came to the conclusion that the cementation of iron is possible only when the surrounding atmosphere contains 96—99 per cent. of carbon monoxide, for only then does reduction of the gas, with formation of carbide, take place; in an experiment to test this result experimentally, somewhat lower values were obtained.

The action of various reagents on metallic iron may be noted. C. F. Burgess and S. G. Engle[66] find that in normal hydrochloric or sulphuric acid, the rates of dissolution of electrolytic iron, tempered steel, ordinary cast-iron, and soft sheet-iron, are approximately in the ratio 40, 10, 7, and 1, but that a preliminary heating of the electrolytic iron to about 1,000°, followed by slow cooling, reduces it to the same rate as the soft iron. Traces of arsenic in the iron greatly increase the resistance to the action of acids. S. Birnie[67] shows that water itself acts on finely-divided iron at all temperatures between 0° and 100°, hydrogen being evolved, and that the presence of oxide in the iron greatly accelerates the action. Even iron filings in presence of water alone bring about the reduction of nitrobenzene to aniline, according to A. Bruno,[68] who also shows that a quantity of carbon dioxide, shaken for some time with iron filings and water, becomes completely replaced by an atmosphere of hydrogen, with formation of ferrous carbonate. The discussion regarding the rusting of iron and steel has been reopened by W. R. Dunstan,[69] and by W. H. Walker and collaborators.[70] These all refute the assertion that the rusting is due to the presence of carbonic acid. The presence of alkali, however, has an inhibitory action, and the results which seemed to indicate the absence of rusting in absence of carbonic acid were probably due to alkali dissolved from ordinary glass vessels; in Jena glass flasks, without carbonic acid, rusting takes place almost as readily as in free air. Walker accepts the view that the action is really an electrochemical one, and describes the experiment of treating iron with water containing traces of phenolphthalein and potassium ferricyanide; the metal soon exhibits zones of different polarity, becoming red where it is acting as cathode (with evolution of hydrogen), and blue where it is acting as anode (with dissolution of iron). The dissolution stops when enough

[65] *Abstr.*, 1907, ii, 470.

[66] *Ibid.*, 29.

[67] *Ibid.*, 469.

[68] *Ibid.*, 756.

[69] *Proc.*, 1907, **23**, 63.

[70] *Abstr.*, 1907, ii, 875.

hydrogen for polarisation is produced, unless a depolariser (free oxygen, hydroxylamine) is present.

In continuation of the work on the volatility of various metals, referred to in last year's Report, Moissan determined the relative volatilities of nickel and cobalt, a matter of some interest in view of the closeness of their melting points. From the results obtained by heating in an electric furnace with a current of 500 amperes at 110 volts, it appears that nickel is decidedly more volatile than cobalt, 56 grams of the former being driven off in the same time as 19 of the latter. By means of an internally-cooled copper tube the metallic vapours can be condensed in the form of microscopic crystals.

The question as to whether the black precipitate, obtained when solution of sulphide is added to solution of ferric salt, is ferric sulphide or a mixture of ferrous sulphide and sulphur, is answered by H. N. Stokes[71] in favour of the first alternative, and the evidence seems fairly conclusive. By continued boiling with water, the precipitate is converted into ferric hydroxide with evolution of hydrogen sulphide; ammoniacal zinc chloride, which does not act on ferrous sulphide at the ordinary temperature, does so in sealed tubes at 170°, forming ferrous hydroxide and zinc sulphide; with alkaline zinc solution the black sulphide from ferric salt gives a mixture of ferric hydroxide and zinc sulphide. The black precipitate obtained from ferrous salt and alkaline polysulphide also behaves as ferric sulphide.

The complex iron derivatives known as Roussin's salts form the subject of several papers by I. Bellucci and C. Cecchetti,[72] and by L. Cambi.[73] According to the former, they are derivatives of a monobasic acid, $HFe_4(NO_7)S_3$, the anion of which is quite well defined; these authors have described a number of new salts, many of which are exceptionally stable. Most of the salts, when heated with alkali, decompose with formation of derivatives of the simpler acid, $HFe(NO)_2S$, but the tetra-alkyl salts can be boiled with a 50 per cent. solution of potassium hydroxide without undergoing decomposition. The various new compounds, as a rule, form black crystals or crystalline powders, and are stable in absence of light.

The only matters of general interest in connexion with the compounds of nickel and cobalt deal with derivatives of higher oxides. I. Bellucci and S. Rubegni[74] have prepared a definite compound of sodium oxide with a higher oxide of nickel, and to it they give the formula $Na_2O,NiO,2NiO_2$. Bellucci and F. Dominici[75] have prepared potassium cobalto-cobaltite in a crystalline condition by fusing, for three hours, potassium hydroxide with any oxide of cobalt; they show its composition to be $K_2O,CoO,3CoO_2$. A number of complex molybdates have been obtained by C. Friedheim and F. Keller,[76] mostly by oxidation of cobaltous compounds in presence of molybdates by means of ammonium persulphate or of hydrogen peroxide; some can be obtained from permolybdates. One of the ammonium compounds,

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[71] *Abstr.*, 1907, ii, 471.

[72] *Ibid.*, 29, 472, 960.

[73] *Ibid.*, 960.

[74] *Ibid.*, 94.

[75] *Ibid.*, 354.

$$3(NH_4)_2O,CoO,CoO_2,12MoO_3,20H_2O,$$

may serve as an example of the kind of substance produced. The violet-red solution obtained when very concentrated solutions of sodium tartrate, sodium hydroxide, and cobaltous sulphate are mixed, undergoes spontaneous oxidation on exposure to air, and becomes green. In presence of glycerol, the amount of oxygen absorbed corresponds with one molecule for two atoms of cobalt, but the resulting compound corresponds only with the oxidation-stage, Co_2O_3, which requires only one molecule for four atoms of cobalt. It is therefore assumed that the cobalt is first directly raised to the CoO_2 stage, but this then oxidises tartrate as a secondary reaction, and itself becomes reduced to the Co_2O_3 stage. The cobaltous solution rapidly absorbs nitric oxide.

A. Werner has again published several contributions to the chemistry of the complex cobalti-derivatives.[77]

Amongst the platinum metals there is very little of a purely chemical nature to record. A peculiar property of platinum amalgam has been noted by Moissan,[78] and confirmed by P. Lebeau[79]; when an amalgam containing even less than 0·1 per cent. of platinum is shaken with water, or when mercury is shaken with a dilute solution of platinic chloride, a buttery mass is obtained which occupies about five times the volume of the original amalgam; this is unaffected, in general character, by change of temperature either down as low as −80° or up to 100°. By cooling below the freezing point of mercury and then cutting sections of the solid mass, it is found from microscopical examination that the structure consists of small drops of water embedded in the amalgam, corresponding with an ordinary emulsion or lather; the action would therefore appear to be purely physical, and due to surface tension. Many other liquids, and also solutions, form similar emulsions with the amalgam.

The preparation of the platinum metals in the colloidal state, and their properties as catalysts, have been further studied by C. Paal and others.[80] Colloidal osmium products were obtained by reducing alkali osmate mixed with sodium protalbate by means of hydrazine hydrate or of aluminium; this yields colloidal osmic oxide, which, after dialysis, can, with care, be evaporated to dryness. The product, on reduction by hydrogen at 30—40°, yields colloidal osmium, soluble in water and stable towards many agents, but oxidisable in air with formation of tetroxide. The authors find that, as regards the catalysis of hydrogen peroxide, osmium hydrosol is the most active of those prepared by their method, next in order being palladium, platinum, and iridium; for reduction experiments, colloidal palladium is much preferable to platinum.

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[76] *Abstr.*, 1907, ii, 96.
[77] *Ibid.*, 961, 962, 963, 964, 965.
[78] *Ibid.*, 360.
[79] *Ibid.*, 479.
[80] *Ibid.*, 360, 559.

A matter of some practical importance in connexion with electrolytic work is noted by C. Marie,[81] who shows that platinum anodes become slightly oxidised during the electrolysis of solutions of platinum chloride, hydrochloric acid, nitric acid, or sodium hydroxide. The oxide formed does not dissolve in the acids mentioned, but does so if some iodide is also added.

Most of the work concerning compounds of the members of this group deals with complex derivatives. The salts of dihydroxylotetrammineplatinum, $[(OH)_2Pt(NH_3)_4]^{\cdot\cdot}$, have been investigated by A. Werner,[82] and are discussed by him from the point of view of his theories of such compounds; he concludes that the differences observed by Carlgren and Cleve in salts prepared by different methods are due to the occurrence of stable polymorphous modifications, and are not to be referred to stereoisomerism. Unstable compounds derived from palladous chloride and hydroxylamine are described by S. Zeisel and A. Nowak[83]; their composition is $Pd(NH_3O)_2Cl_2$ and $Pd(NH_3O)_4Cl_2$, respectively, and the free base corresponding with the latter can be isolated. The constitution of these compounds is also discussed in the light of Werner's theory.

HUGH MARSHALL.

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[81] *Abstr.*, 1907, ii, 698.

[82] *Ibid.*, 969.

[83] *Ibid.*, 276.

ORGANIC CHEMISTRY—ALIPHATIC DIVISION.

Contact Actions at Elevated Temperatures.

A LARGE number of investigations have been carried out which deal with the decomposition or interaction of gaseous substances at elevated temperatures under the influence of catalysts. The results are generally of a highly descriptive and detailed character, and could not with advantage be abstracted in a form suitable for the present Report. A few examples may, however, be cited in illustration of the general nature of the work.

Kusnetzoff[1] finds that finely-divided aluminium at its melting point, like magnesium, brings about the complete decomposition of methane, ethane, and ethylene into carbon and hydrogen. A part of the carbon is deposited on the surface of the metal, and the remainder combines with the metal as carbide.

Mayer and Altmayer[2] have made a further study of the equilibrium between carbon, hydrogen, and methane at high temperatures in presence of metallic nickel or cobalt. The reaction was studied from both directions, starting, that is, either from methane or from its elements. The methane was prepared from aluminium carbide by action of water, and the carbon employed was that resulting from the decomposition of methane by heat. From their results, they calculate that, at the pressure of one atmosphere, the proportion of methane present at 250° is 98·78 per cent., at 536° it is 51·16 per cent., and at 850°, 1·21 per cent. It is considered improbable that methane could have been synthesised from its elements at 1200° as stated by Bone and Jerdan,[3] and it is suggested that the result obtained by these authors must have been due to impurity in the carbon employed.

von Wartenberg,[4] in agreement with Wallis,[5] finds that cyanogen is not produced at 3500° from carbon and hydrogen, although, according to Nernst's theory, the equilibrium mixture at that temperature should contain 44 per cent. of cyanogen. The same author has also made experiments on the synthetic formation of acetylene. A preliminary experiment gave 0·13 per cent. of acetylene at 1824°, which is much lower than the calculated value.[6]

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[1] *Abstr.*, 1907, i, 669.

[2] *Ibid.*, 457.

[3] *Trans.*, 1897, **71**, 41.

[4] *Abstr.*, 1907, i, 299.

[5] *Ibid.*, 1906, i, 730.

Ipatieff[7] has studied the reduction of various substances by hydrogen at high temperatures in presence of catalysts, and shows that hydrogen and acetone react, in presence of iron or nickel, to give *iso*propyl alcohol, and that the reaction is limited and reversible. It is stated also by the same author[8] that oxides of nickel may bring about the catalytic reduction of various compounds more quickly than reduced nickel.

Sabatier and Mailhe[9] have also studied the reduction of ketones in presence of nickel. They find that diacetyl yields dimethylketol and $\beta\gamma$-butanediol; acetylacetone breaks down, giving a mixture of various compounds, but acetonylacetone is almost quantitatively converted into $\beta\epsilon$-hexylene oxide. The same authors state that carbimides may also be reduced in a similar manner. Ethyl carbimide yields methylethylamine, but mono-, di-, and tri-ethylamine are also produced. Phenylcarbimide gives aniline and methane; phenylcarbamide is also formed presumably by the action of water on the original substance. *iso*-Cyanides, which cannot be directly reduced in the wet way owing to their rapid decomposition by water, may easily be reduced by the catalytic method above mentioned.

These authors[10] also find that, when the vapours of acetic anhydride are mixed with hydrogen and passed over nickel at 180°, the products are acetaldehyde, ethyl acetate, ethyl alcohol, and acetic acid. They consider that acetaldehyde and acetic acid are first produced, and that the former then undergoes further reduction to ethyl alcohol.

Sabatier[11] finds that allyl alcohol is in a similar way easily reduced to propyl alcohol.

Senderens[12] states that when the vapours of ethyl alcohol are passed over animal charcoal at 350°, a mixture is produced of methane, ethylene, hydrogen, carbon monoxide, and a little carbon dioxide. Propyl alcohol yields principally propylene, with some ethane, carbon monoxide, and hydrogen.

Lemoine,[13] using wood charcoal at 350°, obtained, from ethyl alcohol, acetaldehyde and hydrogen.

Senderens[14] also finds that alcohols may be dehydrated to olefines when they are heated with amorphous phosphorus. Ethyl alcohol, for example, at 215—240° gave a mixture containing 95 per cent. of ethylene and 5 per cent. of hydrogen phosphide.

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[6] Compare Pring and Hutton, *Trans.*, 1906, **89**, 1591.

[7] *Abstr.*, 1907, i, 827.

[8] *Ibid.*, 828.

[9] *Ibid.*, 488, 587.

[10] *Ibid.*, 747.

[11] *Ibid.*, 458.

[12] *Ibid.*, ii, 248.

[13] *Ibid.*, 248.

[14] *Ibid.*, i, 577.

Hydrocarbons.

The isomeric octanes, which have been already described, are as follows: (1) *n*-octane; (2) di*iso*butyl; (3) γ-methylheptane, and (4) hexamethylethane (Henry, 1906). L. Clarke,[15] in the course of a study of these hydrocarbons, has now succeeded in synthetically preparing an additional isomeride, namely, δ-methylheptane. By condensing β-iodopentane with ethyl sodioacetoacetate and hydrolysing the product, the ketone, $CH_3\cdot[CH_2]_2\cdot CHMe\cdot CH_2\cdot CO\cdot CH_3$, is obtained; this is reduced to the corresponding secondary alcohol, which by treatment with iodine and phosphorus yields the hydrocarbon specified.

The physical properties of liquid and solid acetylene have been investigated by McIntosh.[16] The density of the liquid at $-79°$ is 0·61, and at $-64·8°$ it is 0·577. At atmospheric pressure, the density would be 0·618 supposing that the substance were still a liquid. This gives a molecular volume of 42·1, whereas the value calculated from Kopp's numbers would be 33. The atomic volume of carbon in liquid carbon monoxide[17] is 22 or 23, and, if it is supposed that one of the carbon atoms in liquid acetylene has this value, the observed volume of the compound will agree fairly well with the calculated number. This result therefore appears to favour the acetylidene formula $C\!:\!CH_2$ of Nef.[18]

Molinari[19] considers that by the behaviour of ozone it is possible to distinguish between double and triple linkings, since the latter, according to his observations, do not absorb ozone. By the same method, he proposes to distinguish between benzenoid compounds which contain a true double linking and those which should be represented by the "centric" constitution. Qualitatively, the test is carried out by simply passing ozonised air through a solution of the substance to be investigated in some inert solvent, and testing the issuing gas for ozone by means of potassium iodide. In some cases, as in unsaturated fatty acids, the test may be applied in a quantitative manner by comparing the "iodine number" and the "ozone number" in the resulting compound; if the two agree, only double linkings are present, but if the former is greater, triple linkings are also indicated. By these methods, the author found that stearolic acid,

$$CH_3\cdot[CH_2]_7\cdot C\vdots C[CH_2]_7\cdot CO_2H,$$

and phenylpropiolic acid, $C_6H_5\cdot C\vdots C\cdot CO_2H$, did not combine with ozone. In the latter acid, therefore, the centric constitution is given to the C_6H_5 group.

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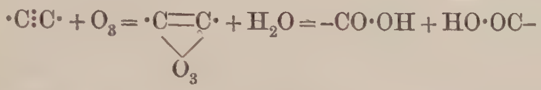
[15] *Abstr.*, 1907, i, 169.
[16] *Ibid.*, 458.
[17] Compare Baly and Donnan, *Trans.*, 1902, **81**, 907.
[18] *Ann. Report*, 1906, 78.
[19] *Abstr.*, 1907, i, 1039.

Harries,[20] however, considers that these results and conclusions are inexact or untrue. His experiments show that certain compounds with triple linkings combine with ozone more rapidly than those with double linkings. He shows further that, contrary to Molinari's statement, both stearolic and phenylpropiolic acids combine with ozone to give ozonides. The disruption of the triple linking by the action of ozone and decomposition of the resulting ozonide may be represented as:



$$\cdot C\vdots C\cdot + O_3 = \cdot\underbrace{C{=}C}_{O_3}\cdot + H_2O = -CO\cdot OH + HO\cdot OC-$$

stearolic acid, for example, giving azelaic and pelargonic acids.

It has been shown by Sir W. H. Perkin that the magnetic rotatory power of hexylene, diallyl, and dipropargyl gave about the normal values, only a slight increase being observed in the value for each unsaturated grouping as the number of such groupings increased. The two acetylene groupings in dipropargyl appeared to behave like four ordinary unsaturated groups; in comparing dipropargyl with its isomeride, benzene, however, it is found that the latter has a much higher value. At first it appeared probable that the higher rotation of benzene was in some way connected with ring-formation, but the abnormally high value which was found for $\Delta^{3:8(9)}$-*p*-menthadiene [21] suggested the possibility that the increase was principally due to the presence of unsaturated groups in conjunction.

In order to test this supposition, the same author [22] considered it desirable to examine some open chain compounds containing unsaturated groups in conjunction, and in the first instance selected for this purpose the simple hexatriene, $CH_2{:}CH\cdot CH{:}CH\cdot CH{:}CH_2$, of van Romburgh and Dorssen.[23]

This hydrocarbon was found to have a remarkably high rotation, the value being 12·196. The difference in the formulæ of hexatriene and benzene is due to ring-formation with loss of two hydrogen atoms, and in the similar case of hexane and hexamethylene the value of this difference was previously found to be 0·982.[24] The value therefore for benzene, obtained by subtraction, is 11·214, which corresponds almost exactly with the experimental value 11·284. This result appears to be in favour of Kekulé's formula for benzene, and it also indicates that the contiguous unsaturated groupings in benzene have the same value as in the open chain compounds.

Miss Smedley [25] has measured the molecular refractions of diphenyl-

[20] *Abstr.*, 1908, i, 75.

[21] Compare Brühl, *Proc.*, 1906, **22**, 319.

[22] *Trans.*, 1907, **91**, 806.

[23] *Abstr.*, 1906, i, 130.

[24] *Trans.*, 1902, **81**, 295.

[25] *Proc.*, 1907, **23**, 295.

butadiene and diphenylhexatriene, and from the data obtained has calculated the influence of the phenyl and ethenoid groups in unsaturated hydrocarbons. In each case, the refractive power of the group increases markedly as the number of unsaturated groups with which it is conjugated increases. The influence of the hexatriene structure is always greater than that of the benzene ring, and it is considered by the author that this result is at variance with the representation of the benzene molecule as a closely conjugated system of double bonds.

Diphenylhexatriene has been prepared by the same author by the condensation of phenyl*iso*crotonic acid with cinnamaldehyde in presence of acetic anhydride. Its solution in benzene exhibits a remarkable blue fluorescence.[26]

Aldehydes and Ketones.

Notwithstanding the large amount of work which has been done on the polymeric modifications of formaldehyde, there is yet much uncertainty and often confusion in designating the individual substances. Auerbach and Barschall[27] have continued their interesting studies on this subject,[28] and the following solid polymerides are classified and described.

Paraformaldehyde is prepared by concentrating a solution of formaldehyde; it is amorphous, colloidal, and contains variable amounts of adsorbed water. Its molecular weight is yet unknown, but is not less than $(CH_2O)_3$. It crystallises in needles or prisms, and melts at 63° (closed tube). Its solution gives none of the ordinary aldehydic reactions, and the compound probably has a cyclic constitution.

α-, β-, γ-, and δ-Polyoxymethylenes are all more or less crystalline and of unknown molecular weight. The first three are obtained by the action of concentrated sulphuric acid, under different conditions, on solutions of formaldehyde; δ-polyoxymethylene is prepared by prolonged heating of the γ-variety with water. The four polyoxymethylenes and paraformaldehyde all tend to pass gradually into simple formaldehyde when dissolved or vaporised.

Orloff[29] considers that in the ordinary method of preparing formaldehyde from methyl alcohol the initial change consists in the decomposition of the alcohol into formaldehyde and hydrogen, and that the formaldehyde itself suffers some decomposition into carbon monoxide and hydrogen. The same author has made a large number of experiments on the influence of various catalysts on the oxidation of methyl alcohol.

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[26] *Proc.*, 1907, **23**, 163.

[27] *Chem. Zentr.*, 1907, ii, 1734.

[28] *Ann. Report*, 1905, 73.

[29] *Abstr.*, 1907, i, 892, 1008.

The present writer[30] finds that carbon dioxide in aqueous solution can be reduced by means of metallic magnesium to formaldehyde. The change is much facilitated by the presence of substances which react with formaldehyde, such as ammonia or phenylhydrazine. Formic acid may, in a similar way, be reduced to formaldehyde, and the reaction may be utilised as a characteristic test for formic acid.[31]

It was shown by Blank and Finkenbeiner, and by Harden, that formaldehyde reacts with hydrogen dioxide in alkaline solution, giving free hydrogen and a metallic formate. Geisow afterwards stated that, if the action takes place in neutral or acid solution, no formic acid is obtained, but only carbon dioxide and hydrogen. The latter statement is now contradicted by Lyford,[32] who finds that formic acid is produced as an intermediate stage and on further action is oxidised to carbon dioxide. The author also states, contrary to Geisow's observation, that barium formate is produced when formaldehyde reacts with barium dioxide.

By the condensation of formaldehyde and acetaldehyde in presence of calcium hydroxide, Tollens and Wigand, in 1892, obtained pentaerythritol, $C(CH_2{\cdot}OH)_4$. This change was considered by Nef to take place in stages, hydracrylaldehyde, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$, $\beta\beta'$-dihydroxy-*iso*butaldehyde, $(HO{\cdot}CH_2)_2CH{\cdot}CHO$, and pentaerythrose,

$$C(CH_2{\cdot}OH)_3{\cdot}CHO,$$

being intermediate compounds. A. F. McLeod[33] has recently endeavoured to obtain experimental proof in favour of this hypothesis, and he has succeeded in showing that, under the influence of very dilute sodium hydroxide solution, a mixture of acetaldehyde and formaldehyde yields considerable amounts of pentaerythrose. The latter compound, it is true, could not be isolated as such, but was converted by reduction into pentaerythritol. The presence of $\beta\beta'$-dihydroxy*iso*butaldehyde was also identified. It is further shown by the author that hydracrylaldehyde[34] and formaldehyde undergo condensation in presence of sodium hydroxide, giving pentaerythrose in almost quantitative yield.

By the interaction of formaldehyde and hydrazine hydrate, Pulvermacher, in 1893, obtained a white, amorphous compound having the formula $(C_2H_4N_2)_x$, which he named "formalazine." It is very insoluble in water, alcohol, or ether, and by the action of acids is readily hydrolysed to the parent substances. Stollé[35] has now made a further study of the reaction in the hope that, under different conditions, it might be possible to obtain triaminotrimethylenetriamine; the latter compound has so far only been isolated in the form of a condensation product with salicylaldehyde.[36] By adding hydrazine hydrate (1 mol.) drop by drop to 40 per cent. formaldehyde solution ($\frac{4}{5}$ mol.) and evaporating on a water-bath, an amorphous product was obtained which is completely soluble in water and which has the empirical composition CH_4N_2. The same product can be obtained by heating trioxymethylene with hydrazine hydrate to 100° in a sealed tube. The author considers that it is a polymerised form of methylenehydrazine, $(CH_2{:}N{\cdot}NH_2)_3$, the silver derivative having the composition $(H_2C{:}N_2H_2)_3,2AgNO_3$. Triaminotrimethylenetriamine does not appear to be formed in the reaction.

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[30] *Trans.*, 1907, **91**, 687.

[31] Fenton and Sisson, *Proc. Camb. Phil. Soc.*, 1908, **14**, [iv], 376.

[32] *Abstr.*, 1907, i, 823.

[33] *Ibid.*, 172.

[34] *Ann. Report*, 1904, 63.

[35] *Abstr.*, 1907, i, 496.

Many different opinions have from time to time been expressed with regard to the formula of metacetaldehyde. Determinations of the molecular weight by means of the vapour density or cryoscopic methods have been made by Friedel, Hanriot and Oeconomides, Troeger, Orndorff and White, and the results pointed to the termolecular formula. The last-named authors considered that paracetaldehyde and metacetaldehyde are to be represented by the same plane formula, and that the difference in their properties is to be explained by stereoisomerism. To paracetaldehyde, this being the more stable modification, the *trans*-configuration was assigned. By keeping metacetaldehyde for a considerable time, they obtained a brittle and opaque modification which was more soluble in phenol or thymol, and the molecular weight of which corresponded to that of tetra-aldehyde.

Zecchini, however, obtained numbers for metacetaldehyde which by the boiling-point method in chloroform agreed with the sexamolecular formula, and by the cryoscopic method, using phenol as solvent, the quadrimolecular formula was approximately indicated.

Hantzsch and Oechslin [37] have made further determinations of the molecular weight in phenol and in thymol solutions by the cryoscopic method, and they conclude that metacetaldehyde exists only in a single form, and is quite stable when pure. Their numbers indicate the quadrimolecular formula when phenol is employed as solvent, and are the same whether the substance is freshly prepared or not. In thymol solution, the compound appears to be sexamolecular. Metacetaldehyde therefore is not isomeric with paraldehyde, but is a higher polymeride.

Raper [38] has studied the condensation of aldol under the influence of a dilute solution of potassium carbonate. The result is shown to be a hydroxyoctaldehyde with a straight chain, since, on oxidation to the corresponding acid and reduction with hydriodic acid, it yields *n*-octoic acid. According to Lieben's rule,[39] it would be expected that the first condensation product should be an aldehyde with a branched chain, which by oxidation and reduction as above would yield α-ethylhexoic acid.

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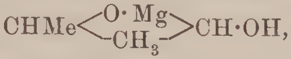
[36] Duden and Scharff, 1895.

[37] *Abstr.*, 1907, i, 1009.

[38] *Trans.*, 1907, **91**, 1831.

[39] *Abstr.*, 1901, i, 449.

Kling and Roy[40] show that when metallic magnesium acts on aliphatic aldehydes in benzene solution, aldol condensation takes place and the resulting aldols are then reduced to glycols. It is supposed that the aldehyde, for example, acetaldehyde, reacts in the two desmotropic forms $CH_3\cdot CHO$ and $CH_2{:}CH\cdot OH$, yielding the intermediate compound,  $CHMe{<}\begin{matrix}O\cdot Mg\\ CH_3\end{matrix}{>}CH\cdot OH$, which is transformed by water into the glycol, $OH\cdot CHMe\cdot CH_2\cdot OH$. In support of this hypothesis, it is stated that aldehydes, such as chloral, in which similar tautomerism is not possible, do not give a similar reaction.

Glyoxal was discovered by Debus in 1856, and was described by him as a colourless, amorphous, and somewhat brittle mass. Böttinger, in 1878, obtained it by Lubavin's method in the form of a yellow syrup, and it appears in this form when prepared from mesoxalic semialdehyde.[41] Although a large number of investigators have been concerned with the reactions and transformations of this substance, its individual properties appear to have been scarcely studied. It now appears from the researches of Harries and Temme[42] that the true unimolecular glyoxal has not hitherto been obtained. Debus's product is considered by these authors to be a polymeride, or a mixture of polymerides, of unknown molecular weight, for which the name polyglyoxal is suggested. They have succeeded, however, in isolating the true unimolecular compound by heating the commercial product with phosphoric oxide. A green gas is obtained, which can be condensed in a well-cooled receiver in the form of beautiful yellow crystals. These melt at 15° to a yellow liquid, which boils at 50°, producing an emerald-green vapour. The vapour can be condensed again to a green liquid, which becomes yellow on cooling, and at 16° solidifies to yellow prisms which, however, become white on strong cooling. The vapour burns with a violet flame, and forms a strongly explosive mixture with air. Analysis and vapour density determination by Victor Meyer's method indicate the simple formula $C_2H_2O_2$. Unimolecular glyoxal can only be kept for a few hours, since it readily undergoes polymerisation, even when placed in a freezing mixture, giving an insoluble modification, $(CHO)_x$, which the authors designate as paraglyoxal. This change occurs immediately in the presence of a small amount of water; if, however, the simple glyoxal is poured into a large quantity of water, it dissolves completely. The solution so obtained contains the compound still in the unimolecular condition, as is evidenced by cryoscopic determination, and by the fact that with phenylhydrazine it yields the well-known glyoxaldihydrazone, melting at 167—168°. The solution is colourless, has a feebly acid reaction, and strongly reduces ammoniacal silver solutions; it does not, however, reduce Fehling's solution.

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[40] *Abstr.*, 1907, i, 586.

[41] *Trans.*, 1905, **87**, 814.

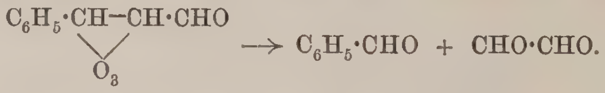
[42] *Abstr.*, 1907, i, 183.

The molecular refraction of glyoxal was found to be 18·86, the calculated value for CHO·CHO being 11·678. An oxymethylene compound of the formula OC:CH(OH) would require the value 12·619.

Brühl points out[43] that, whilst optical exaltation is always observed in the combination C:C·C:O, the group O:C·C:O yields the normal values for the molecular refraction and dispersion. The latter fact is shown to be the case, for instance, in diacetyl, acetylpropionyl, pyruvic acid, and ethyl oxalate; as regards molecular refraction, glyoxal is a further example.

The yellow or green colour of glyoxal is of interest in connexion with the similarity of colour in other compounds containing carbonyl groups in conjunction.[44] Further, it would appear that glyoxal is the simplest coloured compound known which contains only carbon, hydrogen, and oxygen.

When freshly-distilled cinnamaldehyde is dissolved in chloroform and subjected to the action of ozone, an unstable ozonide is obtained, which, when acted on by water, decomposes in the following manner:



$$\underset{O_3}{C_6H_5\cdot CH{-}CH\cdot CHO} \longrightarrow C_6H_5\cdot CHO + CHO\cdot CHO.$$

The resulting solution (after removal of benzaldehyde and benzoic acid by extraction with ether), when evaporated in a vacuum at 25—30°, leaves a yellow mass, which, after drying at 100° over phosphoric oxide, is obtained in the form of an amorphous, friable, yellow substance which dissolves easily in water. Cryoscopic determination shows that in solution this modification is termolecular, but no corresponding derivative can be obtained from it, since in solution it passes quickly into the unimolecular form; phenylhydrazine, hydroxylamine, and sodium bisulphite, for example, yield only derivatives of the latter form. Although in its general properties this termolecular form resembles Debus's product, it differs notably from the latter and from the unimolecular form in that it reduces Fehling's solution. In order to explain this difference, the authors suggest that the termolecular form has been produced by aldol condensation, and has the constitution CHO·CH(OH)·CO·CH(OH)·CO·CHO. The cupric reducing power would then be attributed to the CH(OH) group, and the compound would appear to be related to the sugars.

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[43] *Trans.*, 1907, **91**, 115

[44] Compare, for example, ethyl dioxosuccinate (Anschütz and Parlato, *Abstr.*, 1892, 1181); ethyl oxomalonate (Curtiss, *ibid.*, 1906, i, 480), diacetyl, &c.

Four modifications of glyoxal are therefore known, namely, the unimolecular and termolecular forms, insoluble paraglyoxal, and Debus's polyglyoxal.

It has been previously mentioned that methylglyoxal was isolated by Harries and Türk, but was only obtained in the polymeric form $(C_3H_4O_2)_4$.[45] It appeared probable, however, that by heating this product with phosphoric oxide it might behave like polyglyoxal, and in this way the unimolecular methylglyoxal could be isolated. The present authors find, on making this experiment, that a yellow oil is obtained which emits a green vapour, and that the boiling point of the liquid is higher than that of glyoxal; the yield, however, is only small.

Bacon and Freer[46] have made a further study of the action of sodium on acetone, and they consider that the results confirm their earlier statements.[47] The initial substance is said to be sodium acetone, C_3H_5NaO; it is white, but turns red in the air. When treated with dilute hydrochloric acid, it regenerates acetone, and with ice-cold acetic acid the products are acetone with small quantities of ethyl and *iso*propyl alcohols and pinacone.

Ciamician and Silber have previously shown (1903) that acetone in aqueous solution is decomposed under the influence of sunlight, giving methane and acetic acid. They have now[48] studied the behaviour of some other ketones under similar circumstances, and find that methyl ethyl ketone behaves in the same way, yielding ethane and acetic acid. Lævulic acid gives propionic acid with, probably, formic acid and methyl alcohol.

Dimethylketol or acetylmethylcarbinol, $CH_3{\cdot}CH(OH){\cdot}CO{\cdot}CH_3$, which was discovered by von Pechmann in 1888, is best obtained by the reduction of diacetyl. The most suitable conditions for effecting this reduction and of preparing diacetyl have recently been described by Diels and Stephan.[49] They succeeded in obtaining 1300 grams of pure diacetyl from 4 kilograms of methyl ethyl ketone, and the yield of dimethylketol is 45 per cent. of that required by theory. von Pechmann and Dahl obtained two solid modifications of dimethylketol melting respectively at 126° and 94—98°, but the molecular weights could not be determined, since the substances appeared to undergo de-polymerisation when dissolved. Diels and Stephan now give the melting points as 126° and 85·5°; they find that both modifications can easily be recrystallised; molecular weight determination in boiling acetone indicates that both forms are bimolecular. If, however, these polymeric forms are treated with ether, they lose their power of crystallisation, and tend to pass back to the unimolecular liquid modification. This fact probably explains the somewhat different results of the earlier investigations, since ether was then employed for removing the unchanged dimethylketol.

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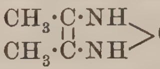
[45] *Ann. Report*, 1905, 74.

[46] *Abstr.*, 1907, i, 479.

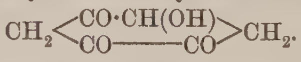
[47] Compare Miss Taylor, *Ann. Report*, 1906, 81.

[48] *Abstr.*, 1907, i, 587.

[49] *Ibid.*, 1000.

Biltz[50] shows that by heating dimethylketol with carbamide in anhydrous acetic acid, dimethylglyoxalone,  $\left.\begin{array}{l}CH_3\cdot C\cdot NH\\ \quad\;\;\, \|\\ CH_3\cdot C\cdot NH\end{array}\right>CO$, is obtained. The properties of this product differ considerably from those of the dimethylglyoxalone which Künne obtained in 1898 from aminomethyl ethyl ketone and cyanic acid. In this compound, the hydrogen atoms in both the imino-groups may be acetylated by means of acetic anhydride in presence of sodium acetate. This appears to be a general rule, the only exceptional case so far recorded being Rupe's monophenylglyoxalone, in which he succeeded in replacing only one of the imino-hydrogen atoms by acetyl. If an imino-group is situated between two carbonyl groups, the basic character of the imino-hydrogen atom is so much diminished that either acetylation is no longer possible, or only very unstable acetyl derivatives are produced. The author cites, amongst other examples, that of parabanic acid, which yields no acetate, and hydantoin, which gives a diacetate easily hydrolysed by water.

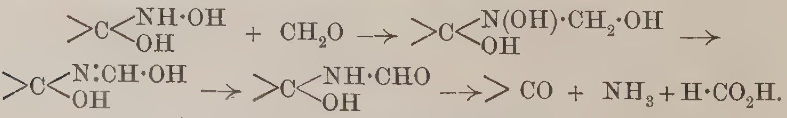
Dimethylketol also condenses with ethyl oxalate, forming a compound, $C_6H_6O_4$, which is probably a hexamethylene derivative,



$$CH_2<\begin{matrix}CO\cdot CH(OH)\\ CO\text{———}CO\end{matrix}>CH_2.$$

It has acid properties, and yields a dihydrazone with phenylhydrazine and a quinoxaline derivative with *o*-phenylenediamine.[51]

Lapworth,[52] in the course of an investigation on the formation and decomposition of oximes in presence of acids, shows that formaldehyde, in presence of concentrated hydrochloric acid, is a most effective agent in removing the hydroximino-groups of ketoximes. The author considers that, in presence of acid, the oximes react as hydroxyhydroxylamine compounds, and that the additive compound formed with formaldehyde then undergoes a transformation analogous to Beckmann's change, yielding formic acid, ammonia, and the ketone:



$$>C<\begin{matrix}NH\cdot OH\\ OH\end{matrix} + CH_2O \rightarrow >C<\begin{matrix}N(OH)\cdot CH_2\cdot OH\\ OH\end{matrix} \rightarrow$$

$$>C<\begin{matrix}N{:}CH\cdot OH\\ OH\end{matrix} \rightarrow >C<\begin{matrix}NH\cdot CHO\\ OH\end{matrix} \rightarrow >CO + NH_3 + H\cdot CO_2H.$$

[50] *Abstr.*, 1908, i, 56.

[51] Diels and Stern, *ibid.*, 1907, i, 466.

[52] *Trans.*, 1907, **91**, 1133.

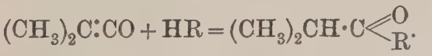
Attention is drawn to the readiness with which oxime formation may take place, in many cases, in presence of concentrated hydrochloric acid, a fact which does not generally appear to be sufficiently recognised. Further, it is shown that when hydroxylamine and formaldehyde react in presence of excess of concentrated hydrochloric acid, a notable quantity of methylamine is produced, the hydroxylamine being therefore reduced by formaldehyde.

The same author and Barrett[53] have studied the influence of acids and alkalis on the velocity of formation of acetoxime. They show that in a solution containing one gram-molecule each of hydroxylamine and acetone in 40 litres at 0°, the velocity of oxime-formation is least when no other base or acid is present. Sodium hydroxide causes a very large acceleration, which is nearly proportional to the concentration. Hydrochloric acid also causes considerable acceleration, the increase being rapid until half a gram-molecule of the acid has been added. Beyond this proportion, the rate diminishes, and attains a nearly constant value when rather more than one molecule of the acid is present.

The properties of dimethylketen, $(CH_3)_2C{:}CO$, have been further studied by Staudinger and Klever.[54] During the preparation of this substance by the method previously described,[55] polymerisation products are obtained, one of which, a solid, appears to be identical with the diketone of Wedekind and Weisswange[56] which was obtained by the action of triethylamine on *iso*butyryl chloride. It is now found that a liquid polymeride is also produced which has the bimolecular formula $(C_4H_6O)_2$, and which differs from the condensation product first mentioned in yielding only a monophenylhydrazone. It has a peppermint-like odour, and yields, by the action of alkalis, an acid which is easily soluble in water.

Dimethylketen combines with tertiary bases to form compounds which are generally very stable, and which differ in this respect from those obtained from diphenylketen and diphenyleneketen. They are formed by union of two molecules of the keten with one molecule of the base.

By combination with the elements of water, alcohol, or amines, dimethylketen gives rise to *iso*butyric acid or its ester or amide respectively:



$$(CH_3)_2C{:}CO + HR = (CH_3)_2CH{\cdot}C{<}^{O}_{R}.$$

Wilsmore and A. W. Stewart have made a study of the behaviour of various organic substances when subjected to the action of a heated platinum wire or of an arc burning between carbon or metallic electrodes. In the cases of ethyl acetate, acetone, and more especially acetic anhydride, a gas was obtained which had a peculiar pungent odour and which could be condensed to a liquid by strong cooling.[57] The first-named author has now continued the investigation,[58] and brings forward evidence to show that the product mentioned is, as previously suggested, keten, $CH_2{:}CO$. Although the substance has not been obtained in a pure condition, the mean results of analysis and molecular weight determinations agree well with this formula. In its properties, the substance behaves as an internal anhydride of acetic acid. With ethyl alcohol, it yields ethyl acetate and with aniline, acetanilide. On standing, especially in the liquid state under pressure, it passes into a brown condensation product.

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[53] *Trans.*, 1908, **93**, 85.

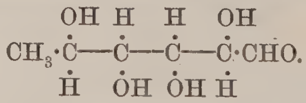
[54] *Abstr.*, 1907, i, 424.

[55] *Ann. Report*, 1906, 83.

[56] *Abstr.*, 1906, i, 437.

Carbohydrates.

Comparatively few papers have been published during the year which deal with the individual sugars. The properties of fucose have been further investigated by Mayer and Tollens[59] with the view of ascertaining its configuration. This methylpentose is, as was first suggested by Votoček, the optical antipode of rhodeose. The authors find that fucose on oxidation with nitric acid yields a trihydroxyglutaric acid, which is probably identical with that obtained by oxidation of *d*-arabinose. By action of hydrogen cyanide, fucose yields the lactone of an acid, fucohexonic acid, which acid on oxidation, unlike the isomeric rhamnohexonic acid, yields no mucic acid. From these results, combined with other evidence, the authors consider that the following configuration of fucose is completely established,



$$CH_3{\cdot}\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}{\cdot}CHO.$$

Raffinose was at one time regarded as an isomeride of lactose, but Loiseau, in 1876, came to the conclusion, from chemical considerations, that it should be classified as a trisaccharide. This view was subsequently confirmed by de Vries, who determined the ratio of the molecular weights of raffinose and sucrose by his well-known "plasmolytic" method. On complete hydrolysis, raffinose yields dextrose, lævulose, and galactose, but by slow "inversion," for example, by means of citric acid,[60] it gives rise in the first instance to lævulose and melibiose.

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[57] *Nature*, 1907, **75**, 510. See also *Proc.*, 1907, **23**, 309.

[58] *Trans.*, 1907, **91**, 1938.

[59] *Abstr.*, 1907, i, 588.

[60] Pieraerts, *Abstr.*, 1906, i, 729.

Neuberg now states[61] that raffinose can be hydrolysed by emulsin, and that the products in this case are galactose and sucrose. This, it would appear, is the first instance in which sucrose has been obtained as a product of the hydrolysis of a more complex natural sugar.

Since emulsin appears to attack only compounds having β-glucoside structures, the author considers that raffinose is to be regarded as the β-galactoside of sucrose or as the lævuloside of melibiose.

An elaborate investigation is being undertaken by Nef on the processes of dissociation in the sugar group, and results are now given[62] of the behaviour of various sugars towards Fehling's solution and other oxidising agents. The author had formerly concluded that the principal oxidation product, in the cases of dextrose and lævulose, was *d*-erythronic acid, but later investigations show that a mixture of monobasic hydroxy-acids is formed, the separation and identification of which has been a matter of considerable difficulty. The action of sodium hydroxide on formaldehyde, diose, trioses, tetroses, pentoses and hexoses was also supposed to yield lactic and erythronic acids. It is now found, however, that no trace of the latter acid is obtained, but that, in addition to lactic acid, a mixture of isomeric 6-carbon saccharins, $C_6H_{10}O_5$, is formed. The question arises whether lower saccharins, $C_4H_6O_3$ and $C_5H_8O_4$, may not also be produced in the case of tetroses, pentoses, &c. Lactic acid is, according to the author, to be regarded as corresponding with a 3-carbon saccharin:

$$C_3H_4O_2 + H_2O \longrightarrow C_3H_6O_3.$$

If, in the reaction under consideration, glyceraldehyde is first produced, the changes may be represented in the following way:

$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO \rightleftharpoons H_2O + {:}CH{\cdot}CH{\cdot}OH{\cdot}CHO \longrightarrow CH_3{\cdot}CO{\cdot}CHO,$$

the resulting methylglyoxal then undergoing an immediate rearrangement analogous to that of benzil to benzilic acid, *r*-lactic acid resulting. The formation of the higher saccharins can be similarly explained. It is shown that when sugars are oxidised in alkaline solution with the oxides of copper, silver, or mercury, saccharins are not produced. Also, that the lower sugars are in this manner directly oxidised and not, as formerly supposed, first converted into higher sugars.

A further account is given by Morrell and Bellars[63] on the compounds of guanidine with various sugars.[64] The general formula for the compounds with dextrose, lævulose, and mannose is

$$3C_6H_{12}O_6{\cdot}2N_3H_5.$$

[61] *Abstr.*, 1907, i, 388.
[62] *Ibid.*, 1908, i, 5.
[63] *Trans.*, 1907, **91**, 1010.
[64] *Ann. Report*, 1905, 85.

They are white, microcrystalline substances, which dissociate to a considerable extent in aqueous solution into their components. Their aqueous solutions show a gradual fall in optical rotation to a minimum value which is the same for the three compounds. The authors consider that this result, in the case of the dextrose and lævulose compounds, represents an apparent equilibrium between two sugars through an intermediate substance X, the concentration of which is very small, $D \longleftrightarrow X \longleftrightarrow L$, the behaviour being analogous to that investigated by Lobry de Bruyn in the action of alkalis on sugars. There is a slow disappearance of X, the intermediate substance, to form acids. When optical equilibrium has been reached, the ratio of lævulose to dextrose remains constant until the formation of acids ceases.

Mention was made in last year's Report (page 91) of Schade's work on the "fermentation" of sugar to alcohol and carbon dioxide without the use of enzymes. The first stage of this operation was supposed to consist in the breaking down of dextrose or lævulose into formic acid and acetaldehyde by the action of alkalis, but subsequent investigation showed that this change is of a different nature, glyceraldehyde being probably formed together with furfural, trihydroxybutyric acid, &c. The same author points out, however,[65] that the second stage, namely, the decomposition of acetaldehyde and formic acid under the catalytic influence of rhodium, has been experimentally confirmed, and that an artificial "fermentation" may be regarded as taking place in the following stages. Dextrose, under the influence of strong alkalis, yields lactic acid (Hoppe-Seyler, Kiliani), and the quantity formed may, according to Duclaux and Schützenberger, amount to 60 per cent. of the weight of sugar taken. Lactic acid, by action of dilute sulphuric acid, yields acetaldehyde and formic acid, and the two latter substances, under the catalytic influence of rhodium, give ethyl alcohol and carbon dioxide. The changes mentioned are in each case brought about by a catalytic agency, and the final result is the breaking down of sugar into alcohol and carbon dioxide.

The much disputed question as to the maximum acylisation capability of cellulose has been further examined by Berl and Watson Smith, jun.[66] Referred to the simplest formula, $C_6H_{10}O_5$, the highest cellulose nitrate is the trinitrate; as regards the acetate, the researches of Green, Ost, and others point to the triacetate as the maximum, whereas Cross and Bevan consider that a tetra-acetate can be produced. The present authors have now studied the formation of aceto-nitrates which are obtained when "nitrocellulose" is treated with acetic anhydride and sulphuric acid. The products obtained vary in composition according to the duration of the experiment, and such compounds as $C_{24}H_{28}O_8(NO_3)_4(OAc)_8$ and $C_{24}H_{29}O_9(NO_3)_2(OAc)_9$ were isolated; in no case was a higher acylated compound obtained. It was not found possible to effect by this process the entire replacement of the NO_3 group by acetyl, but the authors hope to do this in a different way. These aceto-nitrates are more combustible than the acetates, and they react with phenylhydrazine.

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[65] *Abstr.*, 1907, ii, 857.

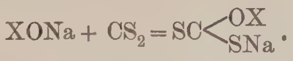
[66] *Ibid.*, i, 289.

Wichelhaus and Vieweg[67] describe experiments which, they consider, favour the view that difference between cellulose and mercerised cellulose is a chemical one. The nitric esters obtained under similar conditions from the two substances named, and containing the same percentage of nitrogen, were found to differ in properties. The yield of benzoate obtained from cellulose before and after mercerisation is also found to be different, being considerably greater in the latter case. The last-named author has also[68] examined the action of sodium hydroxide on cellulose by shaking the material with the alkaline solutions of increasing concentration and titrating the residual liquid. Plotting the amounts of soda taken up by the cellulose against the concentrations, he finds that two horizontal portions occur in the curve which appear to correspond with the values required for the compounds $(C_6H_{10}O_5)_2,NaOH$ and

$$(C_6H_{10}O_5)_2,2NaOH.$$

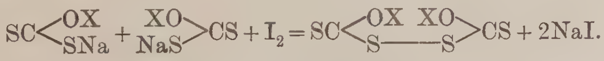
The amount of soda taken up is, within certain limits, proportional to the degree of benzoylation by the Schotten-Baumann method, one molecule of soda being "equivalent" to the introduction of two benzoyl groups. Miller[69] has carried out somewhat similar experiments, and he does not consider that the results obtained can be explained simply by the formation of chemical compounds in fixed proportions.

The xanthogenic esters of cellulose or "cellulose thiocarbonates" have been described in a series of communications by Cross and Bevan (1893—1901). They are obtained by exposing alkali-cellulose hydrate to the action of carbon disulphide at the ordinary temparature, the change being formulated as:



$$XONa + CS_2 = SC{<}\begin{matrix}OX\\SNa\end{matrix}.$$

With iodine, they react in the following way:



$$SC{<}\begin{matrix}OX\\SNa\end{matrix} + \begin{matrix}XO\\NaS\end{matrix}{>}CS + I_2 = SC{<}\begin{matrix}OX & XO\\S & \!\!\!\!-\!\!-\!\!-S\end{matrix}{>}CS + 2NaI.$$

C. F. Cross, Bevan, and J. F. Briggs[70] have now extended these observations to a study on the behaviour of starch when submitted to similar treatment, certain modifications in detail being necessary in

[67] *Abstr.*, 1907, i, 186.

[68] *Ibid.*, 893.

[69] *Ibid.*, 1908, i, 78.

[70] *Trans.*, 1907, **91**, 612.

order to obtain an intimate mixture of the ingredients. The result is a xanthogenic ester of starch, which has a composition analogous to that of the cellulose compound. It is soluble in cold water, and reacts with iodine in the manner above indicated. In aqueous solution, it undergoes hydrolysis, and the authors find that during this spontaneous "reversion" no starch can be detected by the iodine reaction; on the addition of a mineral acid, however, the xanthogenate group is at once decomposed, and the product shows the reactions of starch. The persistence of the SC·SNa group in these products might lead one to regard these residues as measures of the reacting-unit of the carbohydrate. The authors, however, prefer to consider the reacting-unit, in the case of such colloidal complexes, as a system homogeneous with respect to a particular chemical function, although heterogeneous in actual constitution.

It is well known that cellulose which has been bleached without subsequent use of an "antichlor" is found to liberate iodine from potassium iodide even after exhaustive washing. This oxidising property, which is destroyed by boiling with water or by an "antichlor," is considered by Cross and Bevan [71] to be due to a peroxidised derivative of cellulose. Ditz [72] finds that a similar result can be obtained by gradually heating cellulose with an acid solution of a persulphate at 80°. The product, after thorough washing, is found to contain about 0·015 per cent. of active oxygen. It also has acid properties, liberating iodine from a mixture of iodide and iodate; the acid property appears to be distinct from the active oxidising properties, since it is not destroyed by boiling with water. The product is different from the hydralcellulose which Buncke and Wolffenstein obtained by the action of hydrogen dioxide on cellulose. The cellulose peroxide present in the product is stable only for a short time in the moist condition, but may be kept for some weeks when dried over sulphuric acid after treatment with alcohol and ether.

Anhydrides, Acids, and Esters.

In the previous Report (1906, 100), an account was given of the formation and properties of carbon suboxide which was obtained by Diels and Wolf from malonic ethyl ester by action of phosphoric oxide. The subject has now been further studied by Diels and Meyerheim,[73] and it is found that the compound may be produced in a similar way from other esters of malonic acid (for example, dimethyl-, dibenzyl-, and diphenyl-). Oxalacetic ester and methylenetricarboxylic ester when acted on in this way also yield the same carbon suboxide :

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[71] *Zeitsch. angew. Chem.*, 1906, **19**, 2101.

[72] *Abstr.*, 1907, i, 829.

[73] *Ibid.*, 180.

$$C_2H_5{\cdot}O{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}C_2H_5 = CO + 2C_2H_4 + 2H_2O + OC{:}C{:}CO$$

and

$$CH(CO{\cdot}O{\cdot}C_2H_5)_3 = 3C_2H_4 + CO_2 + 2H_2O + C_3O_2.$$

The authors further show, as from the first appeared probable, that carbon suboxide may be obtained by the direct dehydration of malonic acid itself, instead of the ester, by means of phosphoric oxide :

$$CH_2(CO_2H)_2 = 2H_2O + C_2O_3,$$

and this method is now found to be the most suitable for practical purposes. Although a considerable amount of the malonic acid undergoes decomposition into acetic acid and carbon dioxide during this operation, the latter products are easily separated from the carbon suboxide. The acetic acid is mostly retained by the phosphoric oxide being changed into other substances. It is found, in fact, that acetic anhydride can be similarly dehydrated, yielding dehydracetic acid.

Carbon suboxide solidifies, when appropriately cooled with liquid air, to a mass of large, radiating crystals which melt at $-107°$ to $-108°$. When the vapour is passed through a heated tube, it is decomposed with deposition of a metallic-looking mirror, resembling that given by arsenic. Whether this deposit consists of pure carbon or an oxygenated product has not yet been determined. The vapour of carbon suboxide readily undergoes polymerisation at the ordinary temperature, giving a dark red, hygroscopic substance, the change being accelerated by the presence of impurities; when heated to higher temperatures, it breaks up into carbon monoxide and dioxide.

The authors are not inclined to accept the β-hydroxypropiolic-lactone formula for carbon suboxide which was suggested by Michael,[74] and they consider that the physical and chemical properties of the oxide are best represented by the "dioxoallene" formula $O{:}C{:}C{:}C{:}O$ which they originally proposed.

Mixed anhydrides of acetic and boric acids, and of acetic and arsenious acids, have already been obtained by Pictet and his colleagues by direct union of the simple anhydrides. Pictet and Khotinsky[75] now show that acetyl nitrate, $CH_3{\cdot}CO{\cdot}NO_3$, may be similarly obtained. Nitric anhydride is dissolved in acetic anhydride, and the product is purified by distillation under reduced pressure. It is a colourless, fuming liquid, which explodes when quickly heated. In its chemical characters, it closely resembles benzoyl nitrate; the latter, it will be remembered, was isolated by Francis, in 1906, by the action of benzoyl chloride on silver nitrate. It acts as a powerful nitrating agent; benzene, toluene, anthracene, and thiophen can be nitrated by this means below 0°.

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[74] *Ann. Report*, 1906, 102.

[75] *Abstr.*, 1907, i, 175.

Mol[76] has prepared anhydrides of the acid esters of dibasic acids by acting with the acid chlorides on the metallic salts of the esters. The chloride, $COCl{\cdot}CO_2Et$, for example, reacts with the salt,

$$CO_2Et{\cdot}CO_2K,$$

to give the anhydride, $CO_2Et{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CO_2Et$. Similar compounds were obtained from the acid esters of malonic, succinic, and glutaric acids. The compound from oxalic ester on heating is said to yield carbon dioxide and ethyl mesoxalate.

With the object of gaining further information regarding the stability of closed carbon chains, Perkin and Simonsen[77] have carried out investigations on the relative ease with which the *cyclo*propane and *cyclo*butane rings are formed in analogous reactions. The nature of this research and the conclusions arrived at will be discussed elsewhere. In the present section, however, brief mention may be made of an interesting series of acids which the authors obtained while investigating the action of tribromopropane on the sodium derivative of malonic ester. The initial compound is shown to be the ethyl ester of γ-bromoallylmalonic acid,

$$CH_2{:}CBr{\cdot}CH_2{\cdot}CH(CO_2Et)_2.$$

When this is treated with alcoholic potash, it yields a dibasic acid, which has acetylenic properties and which proves to be a butinenedicarboxylic acid, $CH{⋮}C{\cdot}CH_2{\cdot}CH(CO_2H)_2$; this acid is readily decomposed by heat, yielding the monobasic acid,

$$CH{⋮}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

From the latter acid, γγ-dibromo- or iodo-valeric acids may be obtained by treatment with the respective halogen acids.

By acting on the original bromo-ester or on the butinenedicarboxylic acid with hydrobromic acid, acetonylmalonic acid,

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CO_2H)_2$$

is obtained, which melts at 150° with decomposition into lævulic acid and carbon dioxide. The original bromo-ester is only reduced with difficulty, but, when its alcoholic solution is added to molten sodium, allylmalonic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2$, is produced.

Perkin and Prentice, in 1891, when studying the action of methylene chloride on the sodium derivative of malonic ester, obtained as a by-product a yellow, crystalline substance containing sodium. This has now been further investigated by Tutin,[78] who comes to the conclusion that it is the sodium derivative of dicarboxyglutaconic ester. Its formation is probably due to the presence of chloroform as an impurity in the methylene chloride employed.

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[76] *Abstr.*, 1908, i, 76.

[77] *Trans.*, 1907, **91**, 816.

[78] *Trans.*, 1907, **91**, 1141; and *Proc.*, 1907, **23**, 245.

Alkyl substituted tricarballylic acids were obtained by Bone and Sprankling, in 1902, by the interaction of sodium derivatives of cyanosuccinic esters and bromo-fatty acids in alcoholic solution; in this way, the mono- and di-methyltricarballylic acids were prepared and described. Henstock and Sprankling[79] have now extended this method to the preparation of tri- and tetra-methyl derivatives, the initial changes being represented as follows:

$$CO_2Et\cdot CNa(CN)\cdot CHMe\cdot CO_2Et + CMe_2Br\cdot CO_2Et = CO_2Et\cdot C(CMe_2\cdot CO_2Et)(CN)\cdot CHMe\cdot CO_2Et + NaBr$$

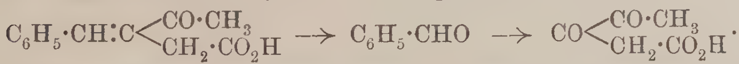
and

$$CO_2Et\cdot CNa(CN)\cdot CMe_2\cdot CO_2Et + CHMeBr\cdot CO_2Et = CO_2Et\cdot C(CHMe\cdot CO_2Et)(CN)\cdot CMe_2\cdot CO_2Et + NaBr.$$

In this way, but using toluene as solvent, the authors obtained $\alpha\alpha\gamma$-trimethyl- and $\alpha\alpha\gamma\gamma$-tetramethyl-tricarboxylic acids. Attempts to convert the trimethyl derivative into a stereoisomeride were not successful.

From ethyl methylsodiocyanosuccinate and ethyl α-bromo*iso*butyrate, the acid, $CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CHMe\cdot CO_2H$, was obtained, which is isomeric with the trimethyltricarballylic acid previously mentioned. Evidence is given to show that the two acids are structurally different, and that they do not represent the two possible inactive forms of the $\alpha\alpha\gamma$-trimethyltricarballylic acid.

Diacetylcarboxylic acid, $CH_3\cdot CO\cdot CO\cdot CH_2\cdot CO_2H$, may be regarded as the intermediate stage, hitherto missing, between diacetyl and diketoadipic (ketipic) acid, $CO_2H\cdot CH_2\cdot CO\cdot CO\cdot CH_2\cdot CO_2H$, since the latter acid yields, as shown by Fittig, diacetyl on dry distillation. Harries and Kircher[80] have now succeeded in the synthesis of this acid by the following interesting method. β-Benzylidenelævulic acid is treated in chloroform solution with ozone, and the resulting wax-like mass, presumably the ozonide, is then decomposed by water. The changes which take place may be represented as follows:



$$C_6H_5\cdot CH{:}C{<}{\begin{matrix}CO\cdot CH_3\\ CH_2\cdot CO_2H\end{matrix}} \rightarrow C_6H_5\cdot CHO \rightarrow CO{<}{\begin{matrix}CO\cdot CH_3\\ CH_2\cdot CO_2H\end{matrix}}.$$

The benzaldehyde (and benzoic acid) is removed by extraction with ether, and the aqueous solution on evaporation in a vacuum yields the diacetylcarboxylic acid as a thick, yellow oil. The acid is fairly stable, and is not decomposed by continued heating with water. It yields a characteristic, green copper salt, a bisphenylhydrazone, and a bis-semicarbazone. A crystalline oxime could not be obtained; its behaviour in this respect is therefore different from that of the isomeric acid, $CHO\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, which Wolff obtained from dibromolævulic acid.

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[79] *Trans.*, 1907, **91**, 354.

[80] *Abstr.*, 1907, i, 466.

It has previously been shown by Le Sueur[81] that certain monohydroxy-acids, when heated to about 270°, decompose into an aldehyde containing one carbon atom less than the parent acid and carbon monoxide:

$$\mathrm{R{\cdot}CH(OH){\cdot}CO_2H \longrightarrow R{\cdot}CHO + CO + H_2O.}$$

This reaction affords a convenient method of preparing certain aldehydes and of systematically degrading a series of acids. The author has now extended these observations to the dihydroxy-derivatives of dibasic acids and shows that an analogous decomposition takes place. When, for example, dihydroxysebacic acid, or its diacetyl derivative, is heated at about 250°, it yields the dialdehyde of suberic acid:

$$\mathrm{CO_2H{\cdot}CH(OH){\cdot}[CH_2]_6{\cdot}CH(OH){\cdot}CO_2H \longrightarrow}$$
$$\mathrm{CHO{\cdot}[CH_2]_6{\cdot}CHO + 2CO + H_2O.}$$

This dialdehyde was previously obtained by Baeyer, in 1897, by oxidising the barium salt of dihydroxysebacic acid with lead dioxide and phosphoric acid. It dissolves in water to form a stable solution, but is itself very readily polymerised, yielding a semi-transparent solid. On oxidation, it gives suberic acid.

The same author[82] finds that when the bromine atoms in $\alpha\alpha'$-dibromoadipic acid are replaced by hydroxyl, two different dihydroxyadipic acids are obtained. Since two asymmetric carbon atoms are present, the author considers that possibly these two acids may be stereoisomerides.[83]

With the initial object of synthetically preparing glutaric acid, Zelinsky and Gutt[84] have studied the behaviour of trimethylene bromide in ethereal solution towards magnesium, and the result is not altogether that which was to be expected. A violent reaction sets in, trimethylene and propylene are evolved, and a product is left which when acted on by carbon dioxide and subsequently hydrolysed yields suberic acid. The authors represent the change as follows:

$$\mathrm{2Br{\cdot}[CH_2]_3{\cdot}Br + 3Mg \longrightarrow BrMg{\cdot}[CH_2]_6{\cdot}MgBr + MgBr_2 \longrightarrow}$$
$$\mathrm{CO_2H{\cdot}[CH_2]_6{\cdot}CO_2H.}$$

Willstätter and Veraguth[85] state that a good yield of suberic acid is obtained when either *cyclo*octane or β-*cyclo*octane is oxidised by nitric acid; β-methyladipic acid is formed also.

The lactone of hydroxycrotonic acid, $\overline{\mathrm{CH_2CH{:}CH{\cdot}CO}}$, was prepared by Lespieau from βγ-dichloro- or dibromo-butyric acids by the action of aqueous potassium carbonate. The same author subsequently showed that this lactone when oxidised with barium permanganate yields the lactone of erythric acid, $\overline{\mathrm{CH_2 \cdot CH(OH) \cdot CH(OH) \cdot CO \cdot O}}$. It is now found that the latter product is a racemic mixture which can be to some extent separated by means of the brucine salts. When the lactone is reduced by means of sodium amalgam in slightly acid solution and the product is kept for some months, crystals are obtained which prove to be identical with natural erythritol.

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[81] *Ann. Report*, 1905, 90.
[82] *Proc.*, 1907, **23**, 196.
[83] Compare Rosenlew, *Ann. Report*, 1904, 72.
[84] *Abstr.*, 1907, i, 676.
[85] *Ibid.*, 303.

An important addition to our knowledge of the constitution of oxalacetic acid is furnished by the recent work of Wohl.[86] It has generally been the custom to represent this acid and its esters by the ketonic formula of Wislicenus, and this constitution, it is true, is consistent with its modes of formation and principal transformations. But evidence has not been wanting, on the other hand, which indicates an enolic structure, and the problem assumes therefore much the same aspect as that met with in other familiar cases of tautomerism, such as that of acetoacetic ester. Brühl, in 1894,[87] from spectrometric measurements, came to the conclusion that oxalacetic ester must have the constitution of hydroxyfumaric or hydroxymaleic ester, and a similar result was arrived at by Drude[88] from observations of the absorption of electric vibrations of high frequency. Michael[89] has shown that methyl oxalacetate exists in two forms, but he yet prefers the ketonic formula and does not consider that the difference depends on a fumaroid and maleinoid configuration.

Nef, in 1893, by the saponification of ethyl ethoxyfumarate, obtained an acid, melting at 172°, which appeared to be hydroxyfumaric acid. Further, it was briefly stated by Michael and Bucher[90] that free oxalacetic acid results from the action of water on acetoxymaleic anhydride or from oxalacetic ester by the action of hydrochloric acid, but the properties of the acid were not mentioned.

Later it was shown[91] that oxalacetic acid may be obtained by oxidation of malic acid in presence of ferrous iron. The product prepared in this way melted at 176—180°, and its properties, which were exhaustively studied, coincided well with the ketonic formula, although the enolic constitution was by no means excluded.[92]

Wohl and Oesterlin[93] subsequently observed that diacetyltartaric anhydride, when treated with pyridine at 0°, yields the pyridine "salt" of hydroxymaleic anhydride,

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[86] *Abstr.*, 1907, i, 583, 584.

[87] *J. pr. Chem.*, [ii], **50**, 119.

[88] *Abstr.*, 1897, ii, 537.

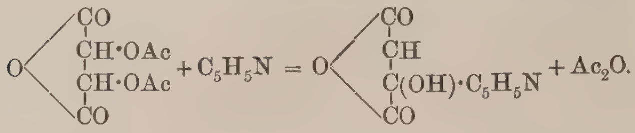
[89] *Ibid.*, 1906, i, 179.

[90] *Ibid.*, 1896, i, 599.

[91] Fenton, *Brit. Assoc. Report*, 1899; Fenton and Jones, *Trans.*, 1900, **77**, 77.

[92] *Loc. cit.*, 83.

[93] *Abstr.*, 1901, i, 365.



When this pyridine compound was acted on by dilute (12 per cent.) sulphuric acid and the mixture extracted with ether, an acid was obtained which appears to coincide in all respects with that which is prepared by the above-mentioned methods, except that it melted at 146° instead of 176—180°. But, by treating the product with 30 per cent. sulphuric acid, the authors succeeded in transforming it into the modification melting at the higher temperature. The reverse transformation can be effected by heating an aqueous solution of the higher melting acid with pyridine at 40—50°. Both of these modifications give at once an intense red colour with ferric chloride, and their solutions, in water or in acetone, immediately decolorise potassium permanganate. The molecular refractions of the two acids are nearly identical, and agree, on the whole, better with the enolic than with the ketonic formula. The molecular heat of combustion at constant volume, however, is greater for the lower melting acid. The affinity constants for the higher and lower melting acids respectively are 0·276 and 0·25, numbers which differ very greatly from the value obtained by H. O. Jones and Richardson for "oxalacetic acid."[94] This difference, the authors considered, is due to the presence of oxalic and acetic acids in the solution employed in the earlier determination.

Taking these and other results into consideration, Wohl arrives at the conclusion that the product of high melting point is hydroxyfumaric acid (m. p. 184°), and the other, hydroxymaleic acid (m. p. 152°). He considers it probable that the salts have the ketonic constitution and that, on acidification, the more labile hydroxymaleic acid is first formed according to Ostwald's rule.

Wohl and Freund[95] have found that the pyridine compound above-mentioned, when acted on by dry hydrogen chloride in ether, minute precautions being taken to exclude moisture, yields the anhydride of hydroxymaleic acid. This is a crystalline, extremely hygroscopic substance, and is converted into hydroxymaleic acid by the action of water.

By the reduction of ethyl oxalate with sodium amalgam, Lörvig, in 1861, obtained the ethyl ester of desoxalic acid to which the constitution $C_2H(OH)_2(CO_2Et)_3$ was assigned. It was afterwards shown by Debus that racemic and glycollic acids, as esters or salts, are also produced when the reduction is carried out in alcoholic solution. This reduction has now been further studied by W. Traube.[96] Instead of treating the reaction-product with water, as was previously done, the author acidifies it with alcoholic hydrogen chloride, and, after removal of the sodium salt, submits the liquid to fractional distillation. He is able to prove the formation of the following ethyl esters: desoxalic, racemic, glycollic, glyoxylic, oxomalonic, $CO(CO_2Et)_2$, and diethylglyoxylic, $HC(OEt)_2{\cdot}CO_2Et$. The last-named ester is not produced directly, but results from the action of the hydrogen chloride on the alcoholate of glyoxylic ester, $CH(OH)(OEt){\cdot}CO_2Et$.

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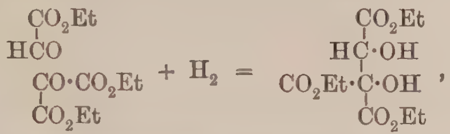
[94] *Trans.*, 1902, **81**, 1158.

[95] *Abstr.*, 1907, i, 584.

In order to explain the formation of desoxalic ester, the author suggests that one molecule each of glyoxylic ester and oxomalonic ester condense with addition of two atoms of hydrogen:



$$\begin{array}{l}\mathrm{CO_2Et}\\ \;|\\ \mathrm{HCO}\\ \mathrm{CO{\cdot}CO_2Et}\\ \;|\\ \mathrm{CO_2Et}\end{array} + H_2 = \begin{array}{r}\mathrm{CO_2Et}\\ |\;\;\;\;\;\\ \mathrm{HC{\cdot}OH}\\ |\;\;\;\;\;\\ \mathrm{CO_2Et{\cdot}C{\cdot}OH}\\ |\;\;\;\;\;\\ \mathrm{CO_2Et}\end{array},$$

the process being analogous to the condensation with reduction of two molecules of glyoxylic acid to racemic acid.

Glyoxylic acid, in the form of its ester, &c., appears to be the principal product in the above-named reduction of oxalic ester, and the process is recommended as a convenient method for its preparation. Reference is also made to the bearing which this reduction has on the question of assimilation in plants, and simple explanations, based on well-established changes, are offered of the building up of many of the best known plant acids.

The author further shows that glyoxylic ester and malonic ester in presence of acetic anhydride condense to give the ethylenetricarboxylic ester of Perkin and Bishop,[97] and that the latter on hydrolysis gives rise to fumaric acid and to malic acid.

Reference was made [98] to Grün's investigations on the synthesis of glycerides. It was mentioned that in the action of sulphuric acid on glycerol, the disulphate is produced even though the acid is employed in large excess, the two primary alcoholic groups undergoing esterification. This disulphate reacts with fatty acids to give symmetrical $\alpha\alpha$-diglycerides; but by starting with glycerol α-monochlorohydrin, the remaining primary and the secondary alcoholic hydroxyl groups are esterified and the product can yield $\alpha\beta$-diglycerides. Grün and Schacht [99] have continued these experiments, and have prepared a considerable number of synthetic diglycerides and of mixed triglycerides. It is shown that in the preparation of diglycerides from glyceryl disulphate, the yield diminishes as the molecular weight of the acid

[96] *Abstr.*, 1908, i, 75.

[97] *Proc.*, 1891, 7, 41.

[98] *Ann. Report*, 1905, 83.

[99] *Abstr.*, 1907, i, 462.

employed is lower. It is probable that the resulting glycerides tend to unite directly with the free fatty acid, so that further esterification is checked, and that this tendency becomes less as the molecular weight of the acid increases. An additive compound of this kind:

$$OH{\cdot}C_3H_5(O{\cdot}CO{\cdot}C_{13}H_{27})_2,2C_{13}H_{27}{\cdot}CO_2H,$$

has, indeed, been obtained as the principal product in the interaction of glyceryl disulphates and myristic acid.

Duffy, in 1852, and also Heintz, in 1849, supposed that certain glycerides which show double melting points may exist in isomeric forms, and the author now finds that in the triglycerides, β-lauro-α-distearin, β-myristo-α-distearin, and β-myristo-α-dilaurin, two forms exist in each case. One form is easily soluble and of lower melting point, the other less soluble modification having a higher or "double" melting point.

Regarding acetoacetic ester as a homogeneous mixture of the two desmotropic forms, the equilibrium state of which in solution depends on the temperature concentration and nature of solvent, it becomes a matter of interest to study the rate of change from the enolic to the ketonic form, or the reverse, under different conditions. Methods of isolation are, of course, inapplicable for this purpose, and the ferric chloride coloration is, under usual circumstances, inappropriate, since the reagent tends to hasten or even to cause enolisation. Stobbe[1] considers, however, that useful information may be obtained from this colour reaction if the conditions are such that the velocity of isomerisation is small, and, working at very low temperatures (-78°), he has been enabled to compare the velocities in different solvents. When amyl, butyl, ethyl, and methyl alcohols are used as solvents, the rate of change from ketonic to enolic form is greater as the molecular weight of the alcohol is larger. This result indicates that the rate is greater in the less dissociating medium, since the dielectric constants of the alcohols mentioned are in the inverse order, that of methyl alcohol being the greatest.[2] By a similar method of observation, the author comes to the conclusion that the proportion of enolic form is greater in methyl or ethyl alcoholic solutions than it is in the liquid ester itself. This result agrees with the observation of Traube, who studied the change in molecular solution volume with time when the ester is dissolved. Brühl, however, by the optical method, concluded that the ketonic form alone is present, not only in the pure substance, but in its solutions in methyl alcohol, chloroform, or water.

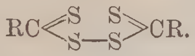
[1] *Abstr.*, 1907, i, 177.

[2] Compare Wislicenus, *Abstr.*, 1896, i, 552; 1900, i, 9; also Federlin, *Abstr.*, 1907, i, 1005.

Stobbe and Ernst Müller[3] have determined the molecular weight of acetoacetic ester by the cryoscopic method, using chloroform as solvent (m. p. −62°), and the result gives numbers agreeing fairly well with the unimolecular formula. The authors consider that the low reaction velocity at the temperature employed in the above-mentioned experiment is therefore due to the temperature only and not to the formation of associated molecules.

Organic acids in which the oxygen of the carboxyl group is entirely replaced by sulphur have already been obtained by Houben and his colleagues; to these compounds, the name "carbithionic acids" is given. They are prepared by the action of Grignard's reagent on carbon disulphide, magnesium phenyl bromide, for instance, yielding phenyl carbithionic acid, $C_6H_5\cdot CS\cdot SH$.

These compounds are stronger acids than their oxygen analogues, and are very unstable. They are easily oxidised by atmospheric oxygen, yielding stable compounds (thioacyl disulphides) of the type:



$$\mathrm{RC}{<}\begin{smallmatrix}\mathrm{S} & & \mathrm{S}\\ \mathrm{S} & - & \mathrm{S}\end{smallmatrix}{>}\mathrm{CR}.$$

So far, only the carbithionic acids of the aryl series had been studied, but Houben and Pohl[4] have now succeeded in obtaining similar aliphatic compounds.

Methylcarbithionic acid, $CH_3\cdot CS\cdot SH$, is prepared by the action of magnesium methyl iodide on carbon disulphide in dry ether and decomposition of the product with hydrochloric acid. It is a reddish-yellow oil, having an intensely disagreeable odour recalling at the same time that of mercaptan, allyl sulphide and acetic acid. It is oxidised by air or by iodine to thioacetyl disulphide.

The constitution of fulminic acid and the conditions of its formation still continue to engage the attention of chemists.[5] Some further investigations in this direction have now been made by Wieland.[6] It was shown by this author and Semper, in 1906, that phenylmethylnitrolic acid, $NO_2\cdot CPh{:}NOH$, very easily decomposes into nitrous acid and the unstable benzonitrile oxide, $C_6H_5\cdot C\vdots N{:}O$, of Werner and Buss. If a similar decomposition should occur in the case of methylnitrolic acid, $NO_2\cdot CH{:}NOH$, one might therefore expect to obtain the yet unknown nitrile oxide, $H\cdot C\vdots N{:}O$, or products of its transformation. Experiment showed, however, that the principal products of its decomposition are formic acid and nitrous oxide, but the author now finds that, under suitable conditions, notable quantities of fulminic acid are also produced. The change here appears to be analogous to that which occurs in the decomposition of chloroformoxime, which was observed by Nef in 1894:

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[3] *Abstr.*, 1907, i, 178.

[4] *Ibid.*, 382.

[5] Compare *Ann. Reports*, 1905, 98; 1906, 100.

[6] *Abstr.*, 1907, i, 196.

$$\mathrm{Cl{\cdot}CH{:}NOH = HCl + C{:}NOH.}$$
$$\mathrm{NO_2{\cdot}CH{:}NOH = HNO_2 + C{:}NOH.}$$

It is considered probable, however, that the unstable nitrile oxide, $\mathrm{H{\cdot}C{\vdots}N{:}O}$, is first produced and then undergoes isomeric change to $\mathrm{C{:}N{\cdot}OH}$.

In the ordinary method of preparing fulminates by oxidation of ethyl alcohol, it is probable, the author considers, that the following series of changes occurs:

$$\mathrm{CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CHO \longrightarrow HC({:}NOH){\cdot}CHO \longrightarrow}$$
$$\mathrm{HC({:}NOH){\cdot}CO_2H \longrightarrow NO_2{\cdot}C({:}NOH){\cdot}CO_2H \longrightarrow}$$
$$\mathrm{NO_2{\cdot}C({:}NOH)H + C{:}NOH + HNO_2 + CO_2.}$$

The principal evidence in favour of this supposition depends on Ponzio's observation (1903) that oximinoacetic acid can be converted into methylnitrolic acid by action of nitrogen peroxide, and on Wohler's statement (1905) that acetaldehyde is a more suitable and a more reactive agent for the preparation of the fulminates than ethyl alcohol.

Palazzo,[7] on the other hand, states that one of the products of the action of nitrous acid on fulminic acid is methylnitrolic acid, that is, nitroformoxime, and considers that this result is in favour of Nef's carbonyloxime formula for fulminic acid.

The older view of Kekulé that fulminic acid has the constitution of nitroacetonitrile has now been generally abandoned. The synthesis of the last-named compound would, however, be a matter of interest, and this has been the subject of several unsuccessful investigations. Scholl, for example, attempted the synthesis by acting with cyanogen bromide on the sodium derivative of nitromethane and by the interaction of silver nitrite and iodoacetonitrile. Steinkopf and Bohrmann[8] have recently attempted to obtain the desired result by other methods, such as the action of phosphoric oxide on nitroacetamide, or that of bromonitromethane on potassium cyanide, but without success.

If cyanoformaldehyde, $\mathrm{CN{\cdot}CHO}$, were obtainable, it might be possible by the action of hydroxylamine to produce from it oximinoacetonitrile, $\mathrm{CN{\cdot}CH{:}NOH}$, and this on oxidation should yield the required nitroacetonitrile. The authors therefore attempted to prepare cyanoformaldehyde by the action of carbon monoxide on hydrogen cyanide, but again without result. They are unable to confirm the statement of Böttinger that hydrogen cyanide is a good solvent for carbon monoxide.

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[7] *Abstr.*, 1907, i, 489.

[8] *Ibid.*, 490.

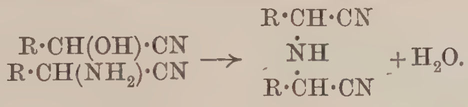
Palazzo and Tamburello[9] have investigated the so-called *iso*cyanuric acid or metafulminic acid which R. Scholl (1896) obtained from mercuric fulminate by action of sodium amalgam. They show that the molecular weight of the acid, as determined by the cryoscopic method in acetic acid, corresponds with the formula $(CNOH)_3$.

Amino- and Imino-compounds.

The mechanism of Strecker's well-known synthesis of amino-acids has been interpreted in various ways by different chemists. Tiemann, for example, considered that the aldehyde unites with hydrogen cyanide, giving a hydroxynitrile, and this is then acted on by ammonia, forming the amino-nitrile. Erlenmeyer, on the other hand, represented the change as consisting in the action of hydrogen cyanide on aldehyde-ammonia, the latter being regarded as an aminohydroxy-compound. The same author showed also that imino-nitriles may be formed in this reaction, presumably as condensation products from two molecules of the amino-nitrile. That ammonium cyanide plays an important part in Strecker's reaction was first suggested by Ljubavin, and has recently been emphasised by the work of Zelinsky and Stadnikoff. The last-named author now[10] gives reasons for considering that the whole change may be represented in the following stages:

(1) $R\cdot CHO,NH_3 + HCN = R\cdot CHO + NH_4\cdot CN$;
(2) $NH_4\cdot CN + H_2O \rightarrow NH_4\cdot OH + HCN$;
(3) $R\cdot CHO + HCN = R\cdot CH(OH)\cdot CN$;
(4) $R\cdot CH(OH)\cdot CN + NH_3 = R\cdot CH(NH_2)\cdot CN + H_2O$.

The formation of the imino-nitrile is represented as:



$$\begin{matrix} R\cdot CH(OH)\cdot CN \\ R\cdot CH(NH_2)\cdot CN \end{matrix} \longrightarrow \begin{matrix} R\cdot CH\cdot CN \\ \dot{N}H \\ R\cdot\dot{C}H\cdot CN \end{matrix} + H_2O.$$

That is to say, the hydroxy-nitrile, behaving as a weak acid, reacts with the amino-nitrile, which, as is known, has basic properties.

The author obtains iminodipropionic acid,

$$CH_3\cdot CH(CO_2H)\cdot NH\cdot CH(CO_2H)\cdot CH_3,$$

by the interaction of α-aminopropionitrile, acetaldehyde, and potassium cyanide and subsequent hydrolysis of the imino-nitrile. The yield was about 73 per cent. of that required by the above theory; had the imino-nitrile resulted from condensation of two molecules of amino-nitrile, the theoretical yield would have been less than the actual quantity obtained.

Ciamician and Silber[11] point out that this iminodipropionic acid is identical with one of the products which they obtained when studying the influence of light on the action of a dilute solution of hydrocyanic acid on aldehyde-ammonia.[12] Stadnikoff also obtains these imino-compounds from the esters of amino-acids and hydroxy-nitriles. Alanine ester hydrochloride, acetaldehyde, and potassium cyanide, for example, yield iminodipropionic acid, and the iminotricarboxylic acid,

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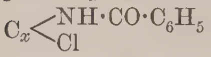
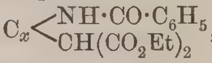
[9] *Abstr.*, 1907, i, 298.

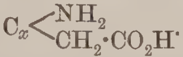
[10] *Ibid.*, 393.

[11] *Ibid.*, 484.

$$CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CH(CH_3)\cdot CO_2H,$$

is similarly obtained from glutamic ester and acetaldehyde.

Schotten's well-known method of obtaining amino-acids from cyclic secondary bases by oxidation of the acyl derivative leads, according to the nature of the acyl group employed, to acids containing the same number of carbon atoms as the base employed or to a lower homologue containing one carbon atom less. J. von Braun[13] now publishes a method by which, from a given cyclic imine, an amino-acid can be obtained containing a larger number of carbon atoms in the molecule. The benzoyl derivative of the cyclic base, $C_x{:}N\cdot CO\cdot C_6H_5$, when acted on by phosphorus pentachloride or pentabromide, yields the chlorinated amide,  $C_x{<}^{NH\cdot CO\cdot C_6H_5}_{Cl}$, and this can then be made to react with either potassium cyanide or with the sodium derivative of malonic ester. In the first case, the nitrile, $C_x{<}^{NH\cdot CO\cdot C_6H_5}_{CN}$, is obtained, which on saponification yields the amino-acid, $C_x{<}^{NH_2}_{CO_2H}$. The product in the second case is the malonic ester derivative,  $C_x{<}^{NH\cdot CO\cdot C_6H_5}_{CH(CO_2Et)_2}$, and this when saponified loses carbon dioxide, giving the acid,



$$C_x{<}^{NH_2}_{CH_2\cdot CO_2H}$$

The resulting amino-acid contains therefore either one or two atoms of carbon more than the original cyclic base according to the mode of treatment.

Piperidine was in this way, by the nitrile process, converted into ε-leucine, $NH_2\cdot[CH_2]_5\cdot CO_2H$, and by the malonic ester treatment to ζ-amino-*n*-heptoic acid, $NH_2\cdot[CH_2]_6\cdot CO_2H$.

Mention has been made in previous Reports (1905, 75; 1906, 107) of the interesting work of Windaus and Knoop, in which it was shown that methylglyoxaline results from the action of zinc hydroxide, in presence of ammonia, on dextrose. The assumption that methylglyoxal is produced and that this is then acted on by ammonia and formaldehyde, is supported by the further observation that, in presence of acetaldehyde, dimethylglyoxaline is obtained.

Windaus has now[14] continued the investigation, and has examined the behaviour of various other sugars when submitted to a similar treatment. Zinc hydroxide, from one part of crystallised zinc sulphate, is dissolved in two parts of 25 per cent. aqueous ammonia, one part of the sugar is added, and the mixture is allowed to stand, in a closed flask, at the ordinary temperature for some months in diffused daylight. Dextrose, mannose, lævulose, sorbose, arabinose, and xylose all yielded methylglyoxaline, and no other ether-soluble base could be detected. Maltose gives a smaller yield than dextrose; with lactose, it is still less, amounting to about one-fifth of that from maltose and one-twentieth of that from dextrose. Sucrose and raffinose give negative results; it would appear in fact that sugars which contain no free carbonyl group do not yield methylglyoxaline.

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[12] *Abstr.*, 1907, i, 19.

[13] *Ibid.*, 524.

[14] *Ibid.*, 288.

When rhamnose is subjected to similar treatment, the result is a mixture of methylglyoxaline and dimethylglyoxaline; from this result, the author concludes that methylglyoxal, formaldehyde, and acetaldehyde must occur as intermediate products.

The action of ammoniacal zinc hydroxide on galactose furnishes a crystalline compound, $C_{12}H_{39}O_{16}N_3Zn$, which reduces Fehling's solution, yields galactosazone with phenylhydrazine, and on oxidation with nitric acid gives rise to mucic acid. It is probably a compound of galactosamines with zinc hydroxide or

$$C_6H_{13}O_5N,C_6H_{16}O_5N_2,4H_2O,Zn(OH)_2.$$

It will be remembered that Lobry de Bruyn and van Leent, in 1895, obtained the compounds $C_6H_{11}O_5\cdot NH_2,NH_3$ and $C_6H_{11}O_5\cdot NH_2$ by the action of ammonia on galactose.

Inouye[15] has also made investigations on the action of ammoniacal zinc hydroxide on sugars other than dextrose, and would appear to have been unacquainted with the last publication of Windaus. He states that both *l*-arabinose and *d*-galactose yield methylglyoxaline. From 150 grams of *d*-galactose, he obtained 15 grams of a zinc compound which, it is stated, yields methylglyoxaline by treatment with hydrogen sulphide, evaporation in a vacuum, and extraction with ether.

The only aminohydroxy-aldehydes which have been known up to the present time are the glucosamines. Wohl and Schweitzer now show that compounds belonging to this class can be obtained from the acetals of unsaturated acids by addition of hypochlorous acid and subsequent replacement of the halogen by the amino-group. Acraldehyde diethyl acetal, $CH_2\colon CH\cdot CH(OEt)_2$, for example, unites with hypochlorous acid, giving chlorohydroxypropaldehyde ethyl acetal,

$$CH_2Cl\cdot CH(OH)\cdot CH(OEt)_2.$$

This compound is only slowly acted on by ammonia, but the action may be greatly facilitated by the addition of potassium iodide. (The general applicability of this reagent in accelerating the replacement of chlorine in double decompositions was pointed out by Wohl,[16] and it is considered probable that an intermediate iodo-derivative is first produced.)

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[15] *Abstr.*, 1907, i, 482.

In the present instance, the methyl acetal was acted on by ammonia in methyl alcohol in presence of sodium iodide. The resulting compound, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH(OMe)_2$, when treated with fuming hydrochloric acid, gives the hydrochloride of aminolactaldehyde, $NH_2 \cdot CH_2 \cdot CH(OH) \cdot CHO,HCl$. It is a crystalline substance, and its aldehydic properties are evidenced by its action on Fehling's solution and ammoniacal silver solution, and the formation of a semicarbazide; bromine water oxidises it to *iso*serine.

Attempts to obtain the free aminohydroxy-aldehyde by acting on the hydrochloride with sodium ethoxide, or with baryta, were not successful. In the case of chitosamine, Breuer, in 1898, showed that the free substance may be obtained from its hydrochloride by action of diethylamine. Applying this method in the present case, it was found that the liberated aldehyde is unstable; reaction occurs between the amino- and aldehydic groups, two molecules of the aminohydroxy-aldehyde condensing with loss of one molecule of water and yielding the stable anhydro-compound:

$$NH_2 \cdot CH_2 \cdot CH(OH) \cdot CH{:}N \cdot CH_2 \cdot CH(OH) \cdot CHO.$$

This product is a white powder, which dissolves easily in water, giving an alkaline solution. Molecular weight determinations by the cryoscopic method led to interesting results. When first dissolved, the numbers obtained corresponded with the termolecular formula, but on allowing the solution to stand the depressions of the freezing point became greater. After three days a bimolecular condition was indicated, and after five days the depression became constant and corresponded with the unimolecular state. This behaviour is very similar to that which was observed in the cases of glyceraldehyde[17] and of glycollaldehyde.[18] The cupric reducing power of the solution also increases as the molecular weight diminishes, but it does not reach its full value unless the substance is first hydrolysed by acids.

Two new synthetical methods of forming *iso*serine are described by Neuberg and P. Mayer.[19] The first method consists in acting on aminoacetaldehyde hydrochloride with hydrogen cyanide in presence of ammonium hydroxide; in the second method, the authors start from $\alpha\beta$-dibromopropionic acid, which by action of silver carbonate is converted into α-bromo-β-hydroxypropionic acid; this, when acted on with ammonia and ammonium carbonate under pressure at 100°, yields

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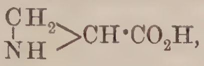
[16] *Abstr.*, 1906, i, 559.

[17] Wohl, *Abstr.*, 1899, i, 11.

[18] Fenton, *Trans.*, 1899, **75**, 575.

[19] *Abstr.*, 1907, i, 295.

*iso*serine. To explain the formation in the way of the β-amino-α-hydroxy-acid, the authors assume the production of an intermediate compound such as  $\begin{matrix}CH_2\\ | \\ NH\end{matrix}\!\!>CH\cdot CO_2H$, which then unites with the elements of water.

It has been shown by Schestakoff[20] that carbamide, when acted on by sodium hypochlorite at a low temperature, yields hydrazine, and that substituted hydrazines may similarly be obtained from substituted carbamides. The change is compared to Hofmann's transformation of amides to amines, the final change representing a removal of the elements of carbon monoxide. In the case of the carbamides, however, there is, at the same time, a linking of the two nitrogen atoms, and it appeared probable therefore that the type of reaction might be extended to similar compounds containing more than two nitrogen atoms. It was not improbable, for example, that biuret might yield 'triazan,' or 'prozan.'

$$NH_2\cdot CO\cdot NH\cdot CO\cdot NH_2 \longrightarrow NH_2\cdot NH\cdot NH_2,$$

the phenyl derivative of which has recently been isolated by Dimroth from the reduction of phenylazoimide. In a similar way, one might possibly expect to obtain 'buzylen'* from hydrazodicarbonamide or azodicarbonamide:

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2 \longrightarrow NH_2\cdot CO\cdot N\colon N\cdot CO\cdot NH_2 \longrightarrow NH_2\cdot N\colon N\cdot NH_2.$$

Working on these lines, Darapsky[21] has studied the action of sodium hypochlorite on the above-named nitrogen compounds and others, and the principal results may be stated as follows. With biuret, only hydrazine is obtained. Semicarbazide is completely decomposed with evolution of nitrogen.

Hydrazodicarbonamide,[22] by similar treatment, yields eventually azoimide. The stages of the operation are represented by the author as follows. Azodicarbonamide is first formed by oxidation, and this partly undergoes hydrolysis, giving the sodium salt of unstable azodicarboxylic acid, $CO_2Na\cdot N\colon N\cdot CO_2Na$. Another part is further oxidised to triazencarbonamide,

$$NH_2\cdot CO\cdot N\colon N\cdot CO\cdot NH_2 \longrightarrow NH_2\cdot CO\cdot N\colon N\cdot NH_2,$$

which, however, undergoes tautomeric change to the corresponding

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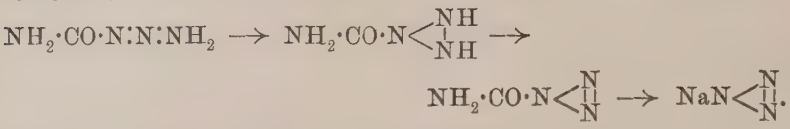
[20] *Ann. Report*, 1905, 95.

* These names were suggested by Curtius for the hypothetical parent substances mentioned. *Ber.*, 1896, **29**, 781, 782.

[21] *Abstr.*, 1907, i, 729.

[22] Thiele, *Annalen*, 1892, **270**, 1; **271**, 128.

*cyclo*triazen; the latter is then oxidised first to carbamazide, which by hydrolysis yields azoimide:



$$NH_2\cdot CO\cdot N\!:\!N\!:\!NH_2 \longrightarrow NH_2\cdot CO\cdot N\Big<\begin{matrix}NH\\ |\\ NH\end{matrix} \longrightarrow NH_2\cdot CO\cdot N\Big<\begin{matrix}N\\ \|\\ N\end{matrix} \longrightarrow NaN\Big<\begin{matrix}N\\ \|\\ N\end{matrix}.$$

Phenylsemicarbazide yields eventually phenylazoimide; as an intermediate stage, phenyltriazen appears to be formed.

Polypeptides.

In the limited space of the present Report, it would be hopeless to attempt to convey an adequate idea of the remarkable progress which has been made by E. Fischer and his colleagues in their researches on the polypeptides. The wide range now covered in this field, and the far-reaching importance of the results, would, indeed, justify the classification of the subject as a separate department. It may be of interest, however, to refer briefly to a few of the more recent results with the object of indicating some of the directions in which the research has developed.

The synthetical process of building up complex polypeptides by linking together, step by step, the residues of amino-acids has been steadily continued. In the previous Report (1906, 112), the isolation of a dodecapeptide, leucyldecaglycylglycine, was announced. In the present year, Fischer has described a tetradeca- and an octadecapeptide,[23] the molecular weight of the latter being higher than that of any synthetical product of known constitution which has yet been obtained. Fischer sees no reason, apart from the cost and trouble, why the process should not be continued to a much higher stage. But it is considered more important to concern oneself with the synthesis of polypeptides from a large number of different amino-acid residues, and which contain, if possible, no contiguous groups of the same kind. Active forms of the amino-acids are to be preferred to the racemic modifications, for the reason that stereoisomerism is excluded; the synthetical process is thus simplified, and the products are more likely to resemble the natural substances.

Four new complex polypeptides are described by Fischer[24] which have been built up from the residues of glycine and *l*-leucine, containing respectively eight, ten, fourteen, and eighteen amino-acid groups. Triglycylglycine, $NH_2\cdot CO\cdot NH\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H$, reacts

[23] "Octadeca" is used in place of "octokaideca" for the sake of uniformity. Compare Fischer, *Ber.*, 1907, **40**, 1755.

[24] *Abstr.*, 1907, i, 485.

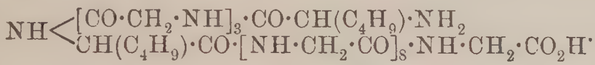
in the cold, in presence of sodium hydroxide, with the chloride of *d*-*a*-bromo*iso*hexoyldiglycylglycine,[25]

$$CHBr(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_2\cdot NH\cdot CH_2\cdot CO_2H,$$

to give *d*-*a*-bromo*iso*hexoylhexaglycylglycine. The latter, when acted on by liquid ammonia, undergoes Walden's rearrangement, and yields the *octapeptide*, *l*-leucylhexaglycylglycine,

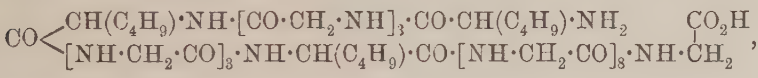
$$NH_2\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_6\cdot NH\cdot CH_2\cdot CO_2H.$$

By starting with pentaglycylglycine in place of triglycylglycine and proceeding in a similar manner, the *decapeptide*, *l*-leucyloctaglycylglycine, $NH_2\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_8\cdot NH\cdot CH_2\cdot CO_2H$, is obtained. This again reacts with the bromo*iso*hexoyldiglycylglycine chloride in presence of soda to give *d*-*a*-bromo*iso*hexoyltriglycyl-*l*-leucyloctaglycylglycine, which, by action of liquid ammonia, is transformed into the *tetradecapeptide*, *l*-leucyltriglycyl-*l*-leucyloctaglycylglycine,



$$NH\left<\begin{array}{l}[CO\cdot CH_2\cdot NH]_3\cdot CO\cdot CH(C_4H_9)\cdot NH_2\\ CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_8\cdot NH\cdot CH_2\cdot CO_2H\end{array}\right.$$

This last-named peptide is then acted on by the bromo*iso*hexoyldiglycylglycine chloride, and the product treated with liquid ammonia as before, when the *octadecapeptide*, *l*-leucyltriglycyl-*l*-leucyltriglycyl-*l*-leucyloctaglycylglycine,



$$CO\left<\begin{array}{l}CH(C_4H_9)\cdot NH\cdot[CO\cdot CH_2\cdot NH]_3\cdot CO\cdot CH(C_4H_9)\cdot NH_2 \qquad CO_2H\\ [NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_8\cdot NH\cdot CH_2\end{array}\right. ,$$

is obtained.

These four polypeptides are all obtained as colourless, indistinctly crystalline powders. The octapeptide is the most soluble in water, and the decapeptide the least soluble. In many of their properties, they so closely resemble the ordinary proteins that they would certainly have been classified as such if they had been found in natural substances. They all give a very strong biuret reaction, and are precipitated by phosphotungstic acid. They do not show the xanthoproteic reaction, nor the reactions of Millon or Adamkiewicz, since they contain neither tyrosine, tryptophan, or cystine. They form sparingly soluble salts with mineral acids. The warm clear solutions of the tetradeca- and octadeca-peptides become opalescent when cold, and are precipitated by a strong solution of ammonium sulphate or by tannic acid. It will be seen from the formula given that the molecular weight of the octadecapeptide is 1213. It is pointed out that if a similar synthesis were carried out with the substitution of the residues of phenylalanine, tyrosine, cystine, &c., for glycyl, the molecular weight of the resulting peptide would be two or three times as great, and would reach the value which has sometimes been assumed for certain natural protein substances.

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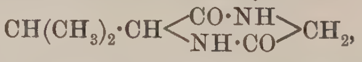
[25] *Abstr.*, 1906, i, 808.

Many polypeptides have been isolated among the decomposition products of natural proteids. From the products of the partial hydrolysis of silk fibroin, for example, glycyl-*d*-alanine and glycyltyrosine have been obtained; in addition to these, a tetrapeptide, probably derived from glycine, alanine, and tyrosine, has been isolated which shows remarkable resemblance to the albumoses. The latter circumstance led Fischer[26] to study some of the higher synthetical polypeptides containing tyrosine, and two such compounds are described which appear to be of great interest. They are *d*-alanylglycyl-*l*-tyrosine and *l*-leucyltriglycyl-*l*-tyrosine. The latter pentapeptide is obtained by acting on *l*-tyrosine with the above-mentioned bromo-*iso*hexoyltriglycyl chloride, and treating the resulting bromo*iso*hexoyltriglycyl-*l*-tyrosine with ammonia. It is easily precipitated from its aqueous solution by ammonium sulphate, and from its slightly acid solution by a concentrated solution of sodium chloride. It is also precipitated by phosphotungstic acid and by tannic acid, and gives a strong biuret reaction and Millon's reaction. In all its properties, in fact, it very closely resembles the albumoses.

The molecular weights of several polypeptides have been determined by the cryoscopic method in aqueous solution. Bearing in mind the fact that glycine yields normal results with this method, it was to be expected that the simpler polypeptides would behave similarly. Although this is generally found to be so, the deviations from the normal are greater than in the case of glycine, and the observed values for the molecular weight are always smaller than those calculated from the formulæ. Triglycylglycine, for instance, gives 178 to 188 instead of 246, but this may possibly be due to the small concentration employed, the substance being sparingly soluble. The diketopiperazine, glycyl-*d*-valine anhydride,



$$CH(CH_3)_2\cdot CH\!<\!\begin{matrix}CO\cdot NH\\ NH\cdot CO\end{matrix}\!>\!CH_2,$$

has a remarkable tendency to separate from its solutions in a gelatinous condition, and one might naturally expect from this circumstance that its molecule would be complex. But the result of cryoscopic determination shows that this is not the case; the value found being 138, whereas the formula given requires 156.

H. J. H. FENTON.

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[26] *Abstr.*, 1907, i, 901.

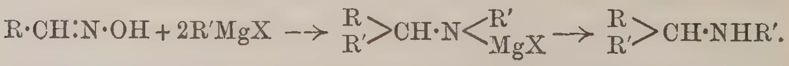
ORGANIC CHEMISTRY—HOMOCYCLIC DIVISION.

In the enormous and continually increasing output of investigations in organic chemistry there is considerable difficulty in recognising and indicating the general lines along which progress is taking place. A large number of the investigations carried out in any given year are isolated in character, having as their object the solution of some immediate problem, without reference, expressed or implied, to any general theoretical scheme. This fact makes it impossible to give a survey of such a field as that of the homocyclic compounds which shall embrace all or even the greater part of the work abstracted during the preceding year. The most that is possible is to select such researches as lend themselves to grouping about a few main lines of investigation, especially such as have a wider bearing than on the special problems under examination. Although there may be differences of opinion as to the relative importance of the various tendencies to be observed in recent work, yet it would seem that certain questions stand out with sufficient prominence to justify their selection.

The problems of the relations between colour and chemical constitution, of the nature of isomeric change in aromatic derivatives, of the structure of the benzene nucleus, and of the conditions of formation of rings, are not only of great intrinsic importance, but their solution is necessary before the fundamental principles of organic chemistry can be regarded as satisfactorily established. Researches into the constitution and synthesis of certain groups such as the terpenes also possess a more than special interest from the remarkable relationships exhibited by some of their members, and from the ingenuity of the methods to which their experimental study has given rise. The diazo-compounds and hydrazones, again, apart from their many practical applications, derive much of their interest from the difficulty of finding formulæ capable of expressing the whole of their chemical behaviour, a difficulty which has led to prolonged controversy. The same may be said of triphenylmethyl, the investigation of which has occupied many workers for a considerable time without entire agreement as to its constitution having yet been reached. It may be said that the insufficiency of purely statical formulæ is being felt more and more acutely, and such conceptions as those of tautomerism and dynamic isomerism are constantly assuming greater importance. That this theoretical change must ultimately lead to a more intimate contact between organic chemistry and physics can hardly be doubted, but at present the points of contact of the two sciences are comparatively few and scattered.

In spite of the increasing use which is made of measurements of such physical constants as the refractive index and magnetic rotation as guides in the determination of structure, the application of physico-chemical methods, especially those of chemical statics and dynamics, to organic problems is still very restricted. Isolated examples during the past year have been the comparative measurement of the velocity of esterification of substituted benzoic acids[1] and an attempt to decide between the possible intermediate products in the oxidation of naphthalene to phthalonic acid by potassium permanganate,[2] and of β-naphthaquinone to phthalic acid by potassium dichromate.[3] The method adopted in each case was to measure the velocity of oxidation, under the given conditions, of each of the compounds which might conceivably appear as an intermediate stage in the reaction. Determinations of the velocity of hydrolysis of esters, &c., when the object is not the study of structure, belong rather to the department of physical chemistry.

There has been no revolutionary introduction of new reagents to record during the past year, and such improvements of detail as need to be mentioned may be treated under their respective sections. The multitudinous applications of Grignard's reaction have been usefully summarised by A. McKenzie in a report laid before the British Association at its Leicester meeting. Among recent applications, the action of Grignard's reagent on oximes has been shown[4] to be the replacement of hydroxyl by alkyl, followed by the formation of an additive compound, which is then hydrolysed:



$$R\cdot CH{:}N\cdot OH + 2R'MgX \longrightarrow \genfrac{}{}{0pt}{}{R}{R'}\!>CH\cdot N<\genfrac{}{}{0pt}{}{R'}{MgX} \longrightarrow \genfrac{}{}{0pt}{}{R}{R'}\!>CH\cdot NHR'.$$

The same product is obtained from the *O*-ethers of the oxime.

Structure of Benzene.

There has been a marked revival of interest in the problem of the constitution of the benzene nucleus, and the relative advantages of the centric and Kekulé formulæ. On the one hand, the properties of ozone as a reagent for the detection of ethylene linkings have been utilised. Unfortunately, the results with benzene itself are as yet inconclusive. The existence of Harries' triozonide of benzene[5] which was cited in support of the Kekulé formula, is denied by Molinari,[6] who finds that benzenoid compounds do not react with ozone, whilst quinonoid derivatives manifest the existence of ethylene linkings in the nucleus by the formation of ozonides. Phenols react as if quinonoid in structure, which is in accordance with many other facts indicating at least the transient existence of the tautomeric form. Theoretical arguments in favour of the centric formula for benzene have also been adduced[7] from the reactions depending on the polymerisation of aliphatic compounds.

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[1] A. Kailan, *Abstr.*, 1907, i, 849; ii, 158, 242, 243, 853.

[2] R. A. Daly, *ibid.*, 1907 i, 407.

[3] M. C. Boswell, *ibid.*, 407.

[4] M. Busch and R. Hobein, *ibid.*, 535.

On the other hand, a body of new facts has recently been brought forward in support of Kekulé's formula. The old objection to it, that it indicated the existence of isomeric ortho-di-derivatives, has now been converted into an argument in its favour. It has been known for some time in technical practice that *o*-nitrotoluene exists in two distinct crystalline modifications, having different melting points. It is now found[8] that these are not merely polymorphic crystalline conditions of the same substance, but that they also differ in the liquid state, having different depression constants, and depositing their corresponding crystals when cooled after long storage in closed vessels. There seems, then, to be some justification for regarding them as true isomerides. Similar modifications have been observed in *o*-chloro- and bromo-toluene, *o*-toluidine, *o*-chlorophenol, *o*-chloroaniline, and 2 : 4-dinitrophenol. Knoevenagel's hypothesis of motoisomerism[9] would call for the existence of isomerides in the para and meta series also, and would even indicate the possibility of two isomeric mono-derivatives when the substituting group is asymmetric, a suggestion which the author considers to derive support from the fact that freshly distilled nitrobenzene has a different viscosity from that which has been kept. Although the facts may be susceptible of more than one explanation, an interesting field of investigation is opened up by them.

There have also been several theoretical attempts[10] to form a conception of the benzene nucleus capable of accounting for the orientation of substituting groups, but the views contained in these papers do not lend themselves to summarisation in a report. In the absence of any clear physical conception of the nature of valency, there is always a danger that theories of the valency of the carbon atom, devised *ad hoc* for the purpose of explaining organic reactions, may

[5] *Ann. Report*, 1906, 120.

[6] E. Molinari, *Abstr.*, 1907, i, 1039.

[7] R. Vidal, *ibid.*, 1020.

[8] I. von Ostromisslensky, *ibid.*, 120, 596 ; E. Knoevenagel, *ibid.*, 202.

[9] *Abstr.*, 1903, i, 785.

[10] J. Obermiller, *ibid.*, 1907, i, 200 ; B. Flürscheim, *ibid.*, 835.

prove on examination to be merely restatements in other language of the problem to be solved.

Colour and Constitution.

The Annual Reports for the last three years have made reference to the growing interest in the question of the relation of colour to structure. The desire to contribute to the solution of this problem has been the motive of a large number of recent researches, and although the relation is still very imperfectly understood, yet within the limits of certain groups it is possible to establish rules for the appearance or non-appearance of colour. It is now generally recognised that a more precise meaning must be given to the idea of colour than has often been the case. The production of physiological colour, due to the occurrence of absorption in the visible spectrum, is more or less an accidental circumstance. Absorption bands may occur in the ultra-violet of equal importance with those in the visible spectrum. In some cases a change in the frequency of the absorbed rays may cause a band to move from the ultra-violet into the visible region without any change of form. A colourless substance may therefore be converted into a coloured one without any real change in constitution having taken place, the alteration in the molecule being only of such a nature as to cause a certain retardation of those oscillations within it which give rise to the absorption.

A study of the colour of a substance thus involves the examination of its entire visible and ultra-violet spectrum,[11] and further, as Hartley and his successors have shown, of the change of absorption with the concentration of the absorbing substance, the results being best expressed in the form of curves. The quantitative study of the absorbing power of a substance, expressed in this manner, makes an exact comparison of different derivatives possible, and relationships are made evident which would escape notice if the examination were confined to visual observations of colour. It is therefore not surprising to find an increasing use of spectroscopic methods in the literature of organic chemistry.

Several different explanations of the origin of colour are offered at the present time, but these explanations are not mutually exclusive, and in the case of certain compounds two or more of the rival hypotheses meet on common ground. From one point of view, colour is ascribed to the presence of a quinonoid structure in the molecule (Armstrong, Gomberg, R. Meyer, and others), from another, to the entrance of certain groups, the auxochromes, into a sensitive molecule, the chromophore (Kauffmann).[12] When a coloured compound is produced from a colourless one, as for instance by solution or by salt-formation, this is explained by a particular form of ionisation (Baeyer) or by a molecular arrangement giving rise to a quinonoid or other linking characteristic of colour (Hantzsch). The more definitely physical theory of Baly regards banded absorption as produced by oscillatory changes of linking within the molecule, due to the conjugation of groups possessing residual affinity. Whilst, therefore, on this view the quinonoid structure is only one phase in an essentially dynamical process, the auxochrome theory is not rejected, but an attempt is made to provide a physical basis for the properties of the auxochromes.

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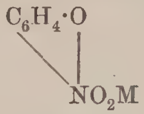
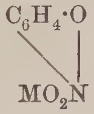
[11] The absorption bands in the infra-red appear to have a different origin, and may be neglected for the purpose of the present discussion.

Nitroquinol dimethyl ether, the colour of which was disputed,[13] has now been shown to be yellow when pure.[14] Its solution in light petroleum is colourless, its other solutions being more and more yellow with increasing dielectric capacity of the solvent.[15] Since both the yellow colour and the molecular weight increase with the concentration, the yellow solutions are regarded as additive compounds. The colour is much less intense than that of nitrophenol salts, and is not considered by Hantzsch to demand the assumption of molecular rearrangement.

A remarkable series of coloured alkali salts of nitro-compounds has been investigated by Hantzsch and his co-workers. Under different conditions of temperature it is possible to obtain both red and yellow salts of the nitrophenols.[16] The product is often orange, consisting of mixed crystals of the two isomerides, which may be separated by crystallisation in absence of water. The red and yellow potassium salts of 2:4:6-tribromo-3:5-dinitrophenol both undergo gradual change in solution until a condition of equilibrium is reached; in other cases one of the salts is only stable at −75°. Structural isomerism is discussed and rejected, the author preferring to represent the two classes of salts as *syn*- and *anti*-stereoisomerides, as:



Red.



Yellow.

Although mononitro-compounds form only colourless salts, dinitro-compounds, such as phenyldinitromethane, yield both red and yellow salts.[17] Both modifications retain their colour when dehydrated, but yield identical equilibrium mixtures in solution, which are found to be unimolecular. The presence of the second nitro-group is necessary, since bromonitromethane and phenylcyanonitromethane,

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[12] For a summary of this question, see H. Kauffmann, "Die Auxochrome," *Ahrens' Sammlung*, 1907, **12**, 1—3. See also J. Schmidt, "Chinone und Chinoide Verbindungen," *ibid.*, 1906, **11**, 10—11.

[13] *Ann. Report*, 1906, 147.

[14] H. Kauffmann, *Abstr.*, 1907, i, 127.

[15] A. Hantzsch, *ibid.*, 513.

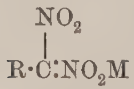
[16] A. Hantzsch, *ibid.*, 207.

$$CN\cdot CHPh\cdot NO_2,$$

form only colourless salts. Evidence is brought forward to show that true *aci*-salts, $R\cdot C{<}^{NO_2}_{NO_2M}$, are colourless. When only one of the nitro-groups is in the methane residue, the other being in one of the phenyl groups, as in the nitrophenylnitromethanes, two colourless and four coloured isomerides are possible. The colourless salts, of which only the mercuric salt of *m*-nitrophenylnitromethane has yet been isolated, would have the formulæ:

$$NO_2\cdot C_6H_4\cdot CH\colon NO_2M \text{ and } NO_2M\colon C_6H_4\colon CH\cdot NO_2.$$

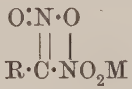
The complete series of four chromo-salts, yellow, red, green, and violet, has been isolated in the case of the potassium salts of *p*-nitrophenylnitromethane. In the formation of the coloured derivatives, both nitro-groups must take part, and the following structures are regarded as the most probable, the dinitroparaffins being selected as the simplest example:



$$\overset{NO_2}{\overset{|}{R\cdot C\colon NO_2M}}$$

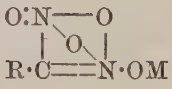
(I.)

Colourless, represented by the ether.



$$\overset{O\colon N\cdot O}{\overset{||\ \ |}{R\cdot C\cdot NO_2M}}$$

(II.)

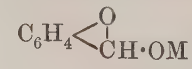


(III.)

Coloured.

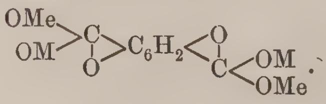
Of these, both (II) and (III) may exist in two stereoisomeric modifications. Isomeric chromo-salts have also been obtained from nitrobarbituric acid and similar compounds.[18] Since, however, the halogenphenols, to which such structural formulæ cannot be applied, yield both coloured and colourless silver salts,[19] the isomerism in question evidently demands further investigation.

It will be observed that the formulæ which Hantzsch now employs to represent the coloured derivatives are not strictly quinonoid, but correspond rather with the "peroxide" formula for quinones. Thus he assigns to the coloured salts of hydroxybenzaldehyde and methyl dihydroxyterephthalate the respective structures:



$$C_6H_4{<}^{\overset{}{O}}_{CH\cdot OM}$$

and



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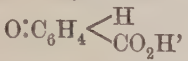
[17] A. Hantzsch, *Abstr.*, 1907, i, 500.

[18] A. Hantzsch, *ibid.*, 555.

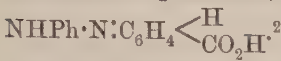
[19] H. A. Torrey and W. H. Hunter, *ibid.*, 1030; A. Hantzsch, *ibid.*, 1908, i, 17.

The fact that these compounds are fluorescent is opposed to a quinonoid structure and indicates the presence of an unaltered benzene nucleus.[20] In connexion with this point it should be mentioned that the tautomeric quinonoid constitution,



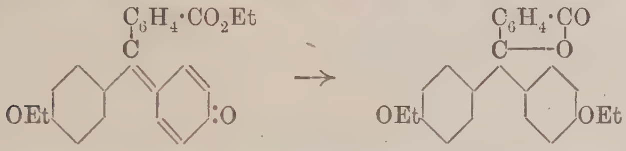
$$O{:}C_6H_4{<}\begin{matrix}H\\CO_2H\end{matrix},$$

has been assigned to salicylic acid in order to explain its production from sodium phenoxide,[21] and its formation of a phenylhydrazone,

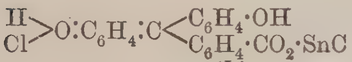


$NHPh{\cdot}N{:}C_6H_4{<}\begin{matrix}H\\CO_2H\end{matrix}.$[22]

By the action of ethyl iodide on the dry silver salts at low temperatures, coloured quinonoid derivatives of phenolphthalein and tetrabromophenolphthalein have been obtained.[23] Hitherto the quinonoid esters have only been prepared by acid alkylation. They readily undergo isomeric change to the colourless lactone ethers :

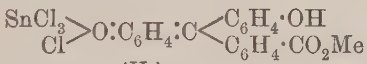


Phenolphthalein forms a red hydrochloride at −30°, which decomposes as the temperature rises, but stable red stannichlorides are readily obtained from phenolphthalein (I), the quinonoid ester (II), and the lactoid dimethyl ether (III) : [24]



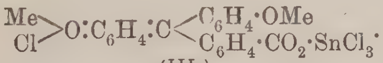
$$\begin{matrix}H\\Cl\end{matrix}{>}O{:}C_6H_4{:}C{<}\begin{matrix}C_6H_4{\cdot}OH\\C_6H_4{\cdot}CO_2{\cdot}SnC\end{matrix}$$

(I.)



$$\begin{matrix}SnCl_3\\Cl\end{matrix}{>}O{:}C_6H_4{:}C{<}\begin{matrix}C_6H_4{\cdot}OH\\C_6H_4{\cdot}CO_2Me\end{matrix}$$

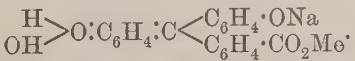
(II.)



$$\begin{matrix}Me\\Cl\end{matrix}{>}O{:}C_6H_4{:}C{<}\begin{matrix}C_6H_4{\cdot}OMe\\C_6H_4{\cdot}CO_2{\cdot}SnCl_3\end{matrix}.$$

(III.)

Similar formulæ are proposed by Green and King, who represent the coloured alkali salts of the ester thus : [25]



$$\begin{matrix}H\\OH\end{matrix}{>}O{:}C_6H_4{:}C{<}\begin{matrix}C_6H_4{\cdot}ONa\\C_6H_4{\cdot}CO_2Me\end{matrix}.$$

It is, however, argued by Baly [26] that such oxonium compounds would be colourless.

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[20] H. Kauffmann, *Abstr.*, 1907, ii, 214, 215 ; A. Hantzsch, *ibid.*, 418.

[21] K. Brunner, *ibid.*, i, 319.

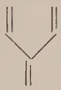
[22] H. Schrötter and J. Flooh, *ibid.*, 929. According to H. Meyer, however (*Monatsh.*, 1907, **28**, 1381), the compound is the phenylhydrazide.

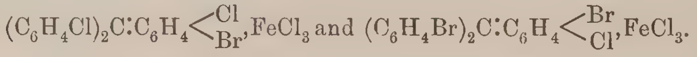
[23] R. Meyer and K. Marx, *Abstr.*, 1907, i, 421, 932 ; H. Meyer, *ibid.*, 625.

[24] K. H. Meyer and A. Hantzsch, *ibid.*, 932.

[25] A. G. Green and P. King, *ibid.*, 933 ; *Proc.*, 1907, **23**, 228.

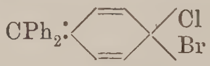
[26] *Proc.*, 1907, **23**, 229.

As in recent years, the battle of the colour theories has been largely fought on the field of the triphenylmethane compounds. Whilst Baeyer considers that quinonoid structures are not the specific cause of colour, but merely facilitate its appearance, since they allow weaker auxochromes to exert their influence, Gomberg now maintains the quinonoid constitution of all the coloured derivatives, modifying it to the extent of considering the grouping  as the only essential part of the quinone ring, since the linking of the upper carbon atom to a bivalent element is absent both from these compounds and from the fulvenes. Gomberg finds[27] that solutions of triphenylmethyl chloride and its derivatives in benzene react with silver sulphate to form coloured sulphates. When para-halogen is present, one atom of this is also removed, which he considers to be evidence of the quinonoid structure. According to Baeyer,[28] however, the slow removal of ring-substituted halogen is due to a destruction of the molecule, as is shown by the fact that an odour of quinone is observed, whereas the diphenylquinomethane, $O{:}C_6H_4{:}CPh_2$, which should be formed on Gomberg's hypothesis, is without odour. The point was tested by a comparison of the ferrichlorides of tri-*p*-chlorotriphenylmethyl bromide and tri-*p*-bromotriphenylmethyl chloride:

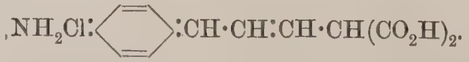


$$(C_6H_4Cl)_2C{:}C_6H_4{<}^{Cl}_{Br},FeCl_3 \text{ and } (C_6H_4Br)_2C{:}C_6H_4{<}^{Br}_{Cl},FeCl_3.$$

The quinonoid portions of the two molecules are identical, and should yield the same halogen with water. The former, however, loses only bromine, and the latter only chlorine. Similar results were obtained with the corresponding stannichlorides by Tschitschibabin,[29] who also found that Gomberg's coloured solutions of the chlorides in liquid sulphur dioxide, heated at 50°, and then decomposed with alkali, gave only chloride without any trace of bromide, whilst the formula



would require the formation of both chloride and bromide. The quinonoid theory is, however, supported by other investigators,[30] and formulæ of this type have been applied to the coloured salts of the *p*-aminocinnamylidene derivatives of acetic and malonic acids,[31] as:



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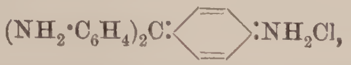
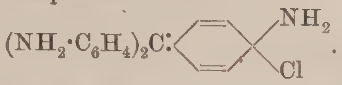
[27] M. Gomberg, *Abstr.*, 1907, i, 504.
[28] A. von Baeyer, *ibid.*, 691.
[29] A. E. Tschitschibabin, *ibid.*, 1022.
[30] F. Kehrmann and F. Wentzel, *ibid.*, 601.
[31] H. Fecht, *ibid.*, 926.

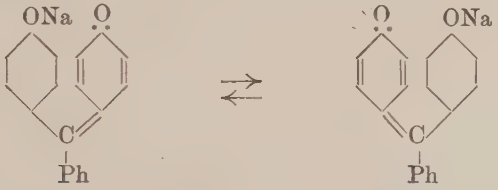
Whilst Gomberg attributes an exactly similar constitution to the salts of pararosaniline with one equivalent of acid :



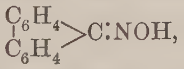
Baker, from a study of their absorption spectra,[32] is led to represent them as carbonium compounds :



An extended study of the hydroxy- and amino-derivatives of triphenylmethane and their salts has led Baeyer (*loc. cit.*) to the conclusion that an oscillation between two forms, similar to that described by Baly as isorropesis, is the origin of the absorption band. If, for instance, two of the benzene rings, *a* and *b*, in triphenylmethane contain each a hydroxyl group, then either *a* or *b* may become quinonoid, and one form may pass into the other without change of properties. In the sodium salt of benzaurin, then, there would be a continuous oscillation between the forms :



In Doebner's violet there would be a precisely similar oscillation of the chlorine between the two NH_2 groups, with corresponding change of linking. The fact that crystal-violet behaves as the salt of a strong monoacid base,[33] whilst the carbinol is only a weak triacid base, is intelligible if the three amino-groups have the same function and are saturated alternately.

The difficulty of finding any statical arrangement of bonds which will invariably produce colour is further illustrated by some investigations of oximes.[34] Phenanthraquinonedioxime and its sodium salt are strongly coloured, but its dimethyl ether, diacyl derivatives, and anhydride are all colourless, although the quinonoid configuration is still intact. Fluorenoneoxime,  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!C\!:\!NOH$, and its sodium salt are coloured, the acyl derivatives are paler, but still yellow, but the methyl ether is actually darker in colour. A comparison of the corresponding derivatives of *o*-benzoquinonedioxime and β-naphthaquinonedioxime[35] has shown that the colour is greatly dependent on the solvent, and the following types of formulæ are suggested:

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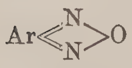
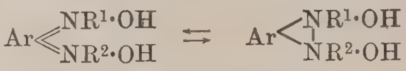
[32] F. Baker, *Trans.*, 1907, **91**, 1490. [33] A. Hantzsch, *Abstr.*, 1900, i, 365.

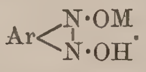
[34] J. Schmidt and J. Söll, *ibid.*, 1907, i, 630, 1054.


$Ar\!<\!\begin{matrix}N\\N\end{matrix}\!>\!O$

Colourless.


$Ar\!<\!\begin{matrix}NR^1\cdot OH\\NR^2\cdot OH\end{matrix} \rightleftarrows Ar\!<\!\begin{matrix}NR^1\cdot OH\\ | \\NR^2\cdot OH\end{matrix}$

Faintly coloured.


$Ar\!<\!\begin{matrix}N\cdot OM\\ | \\N\cdot OH\end{matrix}.$

Strongly coloured.

The influence of substituents, especially hydroxyl, on the isorropesis of quinones has been studied spectroscopically in the case of naphthacenequinone.[36]

Benzoic acid has an absorption band in the ultra-violet, which is also present, though considerably narrower, in the spectra of potassium and silver benzoates. Phthalic acid has a wider band, *iso*phthalic acid has a shallow band in the same position, terephthalic acid does not show a band.[37]

Triphenylmethyl.

The controversy, discussed in previous Reports,[38] as to the constitution of triphenylmethyl still continues. The view that the solid compound is to be regarded as hexaphenylethane, has been criticised as being inconsistent with the stability of tetra- and penta-phenylethane. Pentaphenylethane, however, although stable at the ordinary temperature, becomes unstable when its solution is heated, splitting up into diphenylmethyl and triphenylmethyl groups, which are then readily oxidised.[39] The result found by Hantzsch,[40] who failed to obtain hexanitroethane from iodopicrin, favours the view that the accumulation of negative groups in the ethane molecule tends towards instability. The stable hexaphenylethane, supposed to have been obtained in an impure state from magnesium triphenylmethyl chloride and triphenylchloromethane,[41] is now considered[42] to be impure tetraphenylethane.

Solid triphenylmethyl is colourless, remaining unchanged for several months in dry air.[43] Its solutions are yellow, and hence a different constitution is required for the solid and the dissolved substance. The evidence is now strongly in favour of the hexaphenylethane formula for the solid compound, but no definite conclusion has yet been reached as to its condition in solution. The existing rival views have been summarised by Tschitschibabin.[44]

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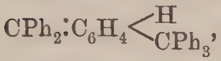
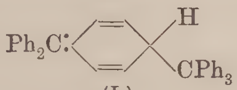
[35] A. Hantzsch and W. H. Glover, *Abstr.*, 1907, i, 1055.
[36] E. C. C. Baly and W. B. Tuck, *Trans.*, 1907, **91**, 426.
[37] W. N. Hartley and E. P. Hedley, *ibid.*, 314, 319.
[38] *Ann. Report*, 1904, 105; 1905, 117; 1906, 131.
[39] A. E. Tschitschibabin, *Abstr.*, 1907, i, 204.
[40] *Ibid.*, 1906, i, 617.
[41] J. Schmidlin, *ibid.*, 1907, i, 27.
[42] Tschitschibabin, *loc. cit.*
[43] A. E. Tschitschibabin, *ibid.*, 691.

(1) "Halochromy," or colour due to ionisation, may be assumed. Thus, in accordance with Baeyer's notation, dissolved triphenylmethyl would be written $CPh_3 \sim\sim CPh_3$. This, however, really only restates the fact without providing any explanation.

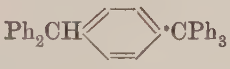
(2) Gomberg suggests that the dissolved substance has the formula  $CPh_2{:}C_6H_4{<}^{H}_{CPh_3}$, which partly dissociates into a quinonoid cation and a benzenoid anion. He does not, however, finally decide between this hypothesis and the existence of the free triphenylmethyl radicle in solution, which is in some ways to be preferred.[45]

(3) Quinonoid formulæ, such as those of Heintschel and Jacobson,[46] may be written for the coloured modification. The final decision between these views is not yet possible.

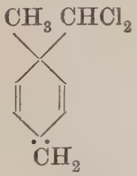
Against the formulæ of Gomberg and Jacobson, it has been urged[47] that the compound (I) would be so unstable as at once to change into the isomeride (II), and in support of this the behaviour of *p*-alkylidenedihydrobenzenes[48] is quoted, the quinonoid configuration in (III) being so unstable as to pass spontaneously into the stable benzenoid form (IV), although in this case the wandering of so heavy a group as $\cdot CHCl_2$ is involved :



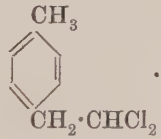
(I.)



II.



(III.)



(IV.)

The magnesium compound of triphenylmethyl chloride has been described[49] as existing in a yellow quinonoid and a colourless benzenoid modification, but the experiments of Tschitschibabin[50] do not confirm the existence of chemical isomerism in this case, as the behaviour of the two preparations is found to be similar, the statement that the yellow form does not yield triphenylacetic acid with carbon dioxide being incorrect.

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[44] *J. pr. Chem.*, 1907, [ii], **74**, 340.

[45] M. Gomberg, *Abstr.*, 1907, i, 514.

[46] *Ann. Report*, 1906, 132.

[47] K. Auwers, *Ber.*, 1907, **40**, 2159.

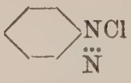
[48] K. Auwers, *Abstr.*, 1907, i, 399.

[49] J. Schmidlin, *ibid.*, 1907, i, 26, 601.

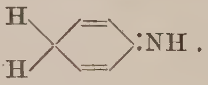
[50] *Abstr.*, 1907, i, 1022.

Diazo-compounds.

The usual representation of diazonium compounds by Blomstrand's formula, and of the diazotates, diazo-cyanides, &c., as stereochemically isomeric azo-compounds, has long been recognised as presenting difficulties. The Blomstrand formula (I) especially fails to indicate the great readiness with which the diazonium salts lose their nitrogen. Since a nitrogen atom directly attached to the benzene nucleus, as in aniline, is generally very firmly retained, it might be expected that diazonium salts would only lose one atom of nitrogen instead of both as is actually the case. The nitrogen atom of aniline is, however, easily removed by oxidation, the product being *p*-benzoquinone. Since this reaction probably proceeds through quinoneimide as an intermediate product, there is some justification for considering that aniline reacts in this case in the tautomeric quinonoid form (II):

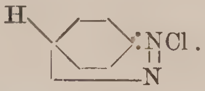


(I.)



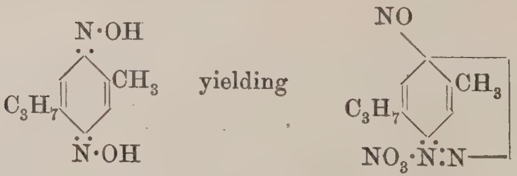
(II.)

These facts have suggested the formulation of diazonium salts as quinonoid derivatives,[51] diazobenzene chloride having the formula



In the elimination of nitrogen, as in the action of water, rupture naturally tends to occur at the double linking. A considerable amount of evidence is adduced in favour of this formula.

Thus the production of a nitrosodiazonium compound by the action of nitrogen peroxide on thymoquinonedioxime,[52] is best accounted for by considering the quinonoid configuration as remaining intact:



Further, whilst *ar*-tetrahydronaphthylamine and 5-aminoquinoline are diazotisable, *ac*-tetrahydronaphthylamine and 4-aminoquinoline, in which the quinonoid formation is no longer possible, do not yield diazo-salts. The non-existence of aliphatic diazonium salts is also accounted for.

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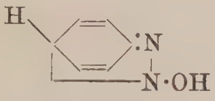
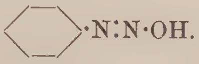
[51] J. C. Cain, *Trans.*, 1907, **91**, 1049.

[52] R. Oliveri-Tortorici, *Abstr.*, 1900, i, 553.

Perhaps a greater difficulty is presented by the metallic diazotates (diazo-oxides) and diazo-cyanides. Cain represents the normal or *syn*-compounds as quinonoid, but having the hydroxyl, &c., attached to the tervalent nitrogen atom (I) and the *iso*- or *anti*-compounds as having the ordinary azo-constitution (II):



(I.)

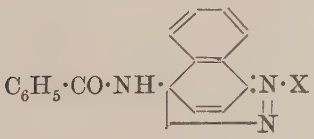


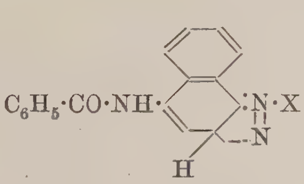
(II.)

This formulation has been but little discussed at present, but it is pointed out that it accords with the different behaviour of the two diazotates towards phenols, the compound (II) having less tendency to couple from its having already the azo-constitution, whereas on Hantzsch's hypothesis the *syn*-compound might be expected to couple less readily than the *anti*- on account of the possibility of steric hindrance:

$$\begin{array}{r} C_6H_5\cdot N \\ OH\cdot\ddot{N} \end{array} \qquad \begin{array}{l} C_6H_5\cdot N \\ \ddot{N}\cdot OH \end{array}$$

The small number of coloured diazonium compounds hitherto known has been increased by the preparation of a remarkably stable series of yellow diazonium salts from benzoyl-1:4-naphthylenediamine.[53] Their aqueous solutions are also yellow, thus differing from the simpler diazonium iodides and thiocyanates, which yield colourless solutions, and were regarded by Hantzsch as owing their colour in the solid state to the presence of the isomeric *syn*-diazo-compound in solid solution. The new salts form neutral solutions, couple readily with alkaline β-naphthol, and yield the nitrosoamine with weak alkalis, and hence can only be regarded as true diazonium compounds. The authors adopt Cain's constitution, representing the salts as either para- or ortho-quinonoid:





An alternative quinonoid structure might be obtained by assuming the presence of a labile hydrogen atom attached to the nitrogen of the benzoylamino-group [54] and wandering to the diazonium nitrogen :

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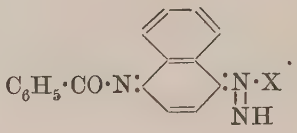
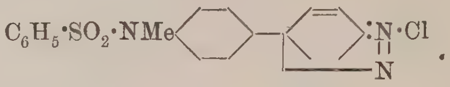
[53] G. T. Morgan and W. O. Wootton, *Trans.*, 1907, **91**, 1311.



In the examination of the diazonium compounds from benzenesulphonylbenzidine and *as*-benzenesulphonylmethylbenzidine,[55] it was found, however, that coloured diazonium halides were obtained from both compounds, although in the second case the labile hydrogen atom is replaced by methyl. The authors therefore adopt the formula :



The nature of the transformation of *s*-trihalogen-substituted diazonium salts of weak acids into quinonediazides [56] has been more fully elucidated by a study of the mixed chlorobromo-derivatives.[57] No difference is to be found in the behaviour of chlorine and bromine, so that in the conversion of the symmetrical 3-chloro-5-bromo-*p*-toluidine, for instance, into quinonediazides, chlorine and bromine are eliminated in equal proportions, the two ortho-positions being equivalent. When halogen is also present in the para-position, the comparison of different chlorobromo-derivatives shows that elimination takes place from the two ortho-positions with equal frequency, and from the para-position with half that frequency, so that the ratio $o:o':p=2:2:1$.

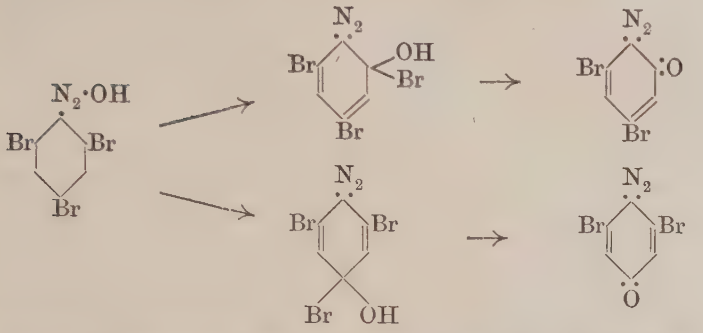
The authors do not incline to accept Cain's formulation of the diazo-compounds. They assume a benzenoid structure for the solid diazonium salts, but consider that an aqueous solution contains *o*- and *p*-quinonoid phases in equilibrium, under such conditions that each ortho-phase occurs twice as often as the para-phase. No explanation of the constancy of this ratio is offered. The quinonoid compounds present in solution are represented as carbonium derivatives, so that the transformation in a particular case may be shown thus, only one of the two ortho-configurations being given :

[54] J. T. Hewitt, *Proc.*, 1907, **23**, 181.

[55] G. T. Morgan and J. M. Hird, *Trans.*, 1907, **91**, 1505.

[56] *Ann. Report*, 1905, 107.

[57] K. J. P. Orton and W. W. Reed, *Trans.*, 1907, **91**, 1554.



Diazonium compounds of this type, although yielding almost exclusively quinonediazides when heated with dilute acids, readily undergo the normal conversion into phenols under the influence of sunlight.[58] This is shown to be entirely a diazonium reaction, not dependent on the intermediate formation of a *syn*-diazohydroxide, as it takes place under conditions unfavourable to hydrolysis, as in 95 per cent. sulphuric acid solution. Solutions of diazotates are very stable when exposed to light. When alcohols or acetic acid are employed as the solvent instead of water, the corresponding ethers or phenyl acetates are obtained, the phenetole formation, for instance, being favoured by the exposure of a suspension of the diazonium salt in alcohol, free from acid, to sunlight.

Among other investigations in the department of diazo-compounds may be mentioned a study[59] of the red oil found by Griess, together with azobenzene, in the product of the action of potassium ferrocyanide on diazobenzene chloride. Since it yields triphenylhydrazine, $NPh_2{\cdot}NHPh$, on reduction, and undergoes the semidine transformation to form aminotriphenylamine, $NH_2{\cdot}C_6H_4{\cdot}NPh_2$, it is regarded as having the constitution $C_6H_4{<}\begin{matrix}NPh\\ |\\ NPh\end{matrix}$. In the case of the diazotoluene salts, the reaction appears to be more complicated.

By the diazotisation of aniline with 0·5 mol. of sodium nitrite in dilute acetic acid solution, an orange isomeride of diazoaminobenzene has been obtained[60] the constitution of which is represented by the formula, $NHPh{\lll}\begin{matrix}NPh\\ |\\ N\end{matrix}$. Its acetic acid solution probably contains a compound, $NH_2Ph{<}\begin{matrix}NPh\\ |\\ N{\cdot}OAc\end{matrix}$, which couples with β-naphthol in the cold, yielding a red colouring matter, whilst diazoaminobenzene only couples on boiling, and gives a yellow product. Cuprous chloride or molecular copper decomposes the compound at the ordinary temperature into phenol, aniline, and nitrogen. The same isomeride is obtained in presence of other organic acids, but the stronger the acid the less tendency is there to form the new compound.

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[58] K. J. P. Orton, J. E. Coates, and F. Burdett, *Trans.*, 1907, **91**, 35.

[59] A. Ehrenpreis, *Abstr.*, 1907, i, 453.

[60] E. I. Orloff, *ibid.*, 365.

The absence of isomerism in the mixed aromatic diazoamino-compounds has frequently been investigated. Since in the usual method of preparation from diazo-salts and amines a considerable part is played by the water and electrolytes present, an attempt has been made[61] to realise the isomerism by the synthesis of unsymmetrical diazoamino-compounds from azoimides and magnesium organic derivatives. The attempt failed, however, the same product being obtained from phenylazoimide and magnesium α-naphthyl bromide, and from α-naphthylazoimide and magnesium phenyl bromide. Several pairs of compounds were examined in the same manner.

Phenylmethyltriazen[62] has been regarded as tautomeric in character, reacting in the two forms $C_6H_5\cdot N\colon N\cdot NHMe$ and

$$C_6H_5\cdot NH\cdot N\colon NMe,$$

the second formula being an indirect inference from its behaviour with acids. Its discoverer has now shown[63] that it and its homologues are only correctly represented by the first formula, as the condensation with diazobenzene salts gives rise to bisdiazoamino-compounds which are always symmetrical, having the constitution $R\cdot N\colon N\cdot NR'\cdot N\colon N\cdot R''$. This is proved by the fact that the product from phenylmethyltriazen and p-diazotoluene chloride is identical, and not isomeric, with that from p-tolylmethyltriazen and diazobenzene chloride.

An interesting preparation of certain aminoazo-compounds, which differs from those usually employed in being additive instead of substitutive, consists in the interaction of the p-diazoimides and active amines.[64] Aniline does not react in this way, but satisfactory results are obtained with the naphthylamines and certain m-diamines. Since monoalkylnaphthylamines react, only less readily, whilst dialkylnaphthylamines do not react, the authors assume that the addition occurs through the intermediate assumption by the amine of a quinonoid configuration :

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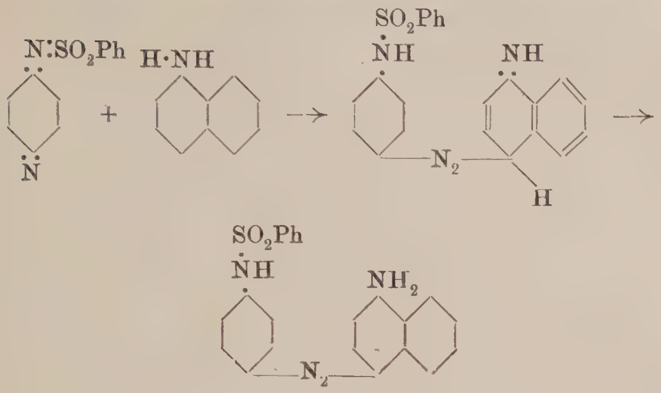
[61] O. Dimroth, M. Eble, and W. Gruhl, *Abstr.*, 1907, i, 664.

[62] *Ann. Report*, 1905, 107.

[63] O. Dimroth, M. Eble, and W. Gruhl, *loc. cit.*

[64] G. T. Morgan and F. M. G. Micklethwait, *Trans.*, 1907, **91**, 1512.



Hydrazones and Hydroxyazo-compounds.

The results of a spectroscopic study of the hydroxyazo-compounds and their derivatives [65] have led to the conclusion that whilst the para-compounds and their hydrochlorides have the azo-constitution, the *o*-quinonehydrazone formula must be assigned to the ortho-compounds and their acyl derivatives. The ethers and hydrochlorides of the ortho-series, on the other hand, show absorption spectra indicating that they have the azo-structure. The spectrum of the hydrochlorides suggests that they are carbonium salts.[66] The hydroxyl or ethoxyl group having some residual affinity, its presence in the benzene nucleus of an azo-compound modifies the spectrum of azobenzene considerably, but when the residual affinity of the substituting group is diminished by replacing the hydroxylic hydrogen by acetyl or benzoyl, the spectrum approaches more nearly to that of azobenzene.

Spectroscopic evidence also goes to show [67] that the phenylhydrazones and osazones exist in neutral solutions in the form of hydrazones, with the exception of phenylgloxalosazone and dextrosazone, which appear to be partly or entirely in the azo-form. But when sodium ethoxide is added to the solutions, a part at least of the substance is converted into the azo-compound. The influence of the presence of neighbouring hydroxyl groups, and of the conjugation of $:C:N\cdot$ linkings, was also studied.

The same problem has also been attacked by a number of workers from the chemical side. In favour of the azo-constitution for the para-compounds is the conversion of *p*-benzoquinonebenzoylphenylhydrazone (I) into benzoxyazobenzene (II) by contact with potassium hydroxide in the cold, a transformation which is also undergone by the substituted derivatives:[68]

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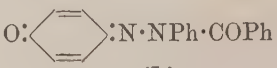
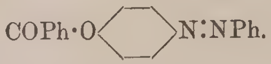
[65] W. B. Tuck, *Trans.*, 1907, **91**, 449.

[66] F. Baker, *ibid.*, 1490.

[67] E. C. C. Baly, W. B. Tuck, E. G. Marsden, and M. Gazdar, *ibid.*, 1572.

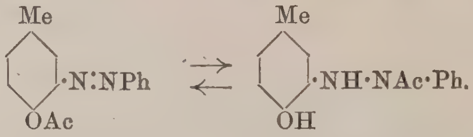


(I.)



(II.)

There is less agreement as to the ortho-compounds. Whilst Tuck considers these to be hydrazones, the whole of the *o*-hydroxyazo-compounds with their ethers and esters are regarded by Auwers[69] as retaining the azo-structure. According to this author, the acetyl derivative of benzeneazo-*p*-cresol is an *O*-derivative. On reduction, it yields the *N*-acetyl derivative of the hydrazo-compound, but it is not possible to obtain the quinonehydrazone on gentle oxidation with ferric chloride or mercuric chloride, as it at once reassumes the azo-configuration:



The product of the action of *as*-benzoylphenylhydrazine on β-naphthaquinone was found also to be an azo-compound, being identical with that obtained by benzoylating β-benzeneazo-α-naphthol. It undergoes reduction to the hydrazo-compound. Auwers thus considers these *O*-benzoyl- and acetyl-derivatives to undergo spontaneously the same change as that observed by Willstätter and Veraguth in the para-series under the influence of potassium hydroxide. Auwers' paper is described as a preliminary note, so that a further experimental investigation of this question may be expected.

A transformation which is in a sense the reverse of that of Willstätter and Veraguth, namely, the isomeric change of azo-compounds into hydrazones, occurs on heating triacylmethanes,[70] the coloured compounds of the constitution $Ac_3C{\cdot}N{:}NPh$ passing into the colourless isomerides $Ac_2{:}N{\cdot}NAc{\cdot}Ph$. The transfer of the labile group here is from carbon to nitrogen. One of the acyl groups in the triacylmethanes is evidently very loosely combined. When acetyl and benzoyl are both present, it is the acetyl group that becomes labile.

The absorption spectra in the visible region of a number of nitrated *p*-hydroxyazo-compounds have been examined with the view of studying their constitution.[71] The *p*-nitroazophenols and their salts exhibit absorptions of radically different type. The authors regard the salts as being *iso*nitro-derivatives, and they are thus represented as quinonoid. This is in accordance with the views of Baly and Tuck [72] on the structure of the *p*-nitrophenylhydrazones of aldehydes and ketones. The quinonoid alkali salts have a purple or blue colour, the absorption being shifted towards the red in comparison with that of the parent compound. The tabulated absorptions indicate that the oscillation frequency is less the longer the chain of alternate double and single linkings in the molecule.

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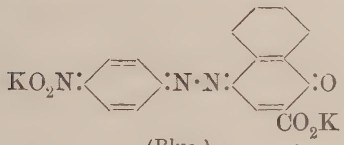
[68] R. Willstätter and H. Veraguth, *Abstr.*, 1907, i, 453.

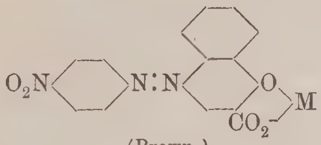
[69] K. Auwers, *ibid.*, 554.

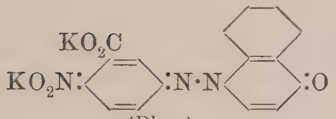
[70] O. Dimroth and M. Hartmann, *ibid.*, 1090.

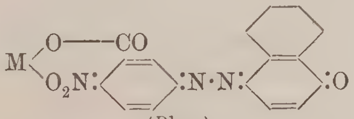
[71] J. T. Hewitt and H. V. Mitchell, *Trans.*, 1907, **91**, 1251.

As the formation of lakes is known to require the presence of two hydroxylic groups (one of which may be carboxyl) in the ortho-position relative to one another, this view of the constitution of the nitro-derivatives was tested by a comparison of the salts of two isomeric carboxylic acids derived from benzeneazo-α-naphthol. Both acids form blue potassium salts, but whereas the one containing OH and CO_2H in the ortho-position gives brown precipitates with salts of the heavy metals, that in which NO_2 and CO_2H are in the ortho-position gives blue precipitates. The quinonoid structure is therefore intact in the latter case, and the compounds are related thus :

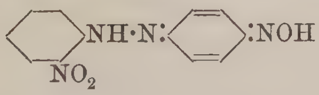

(Blue.)


(Brown.)


(Blue.)


(Blue.)

The nitro-group has a considerable influence on the formation of phenylhydrazones. Thus, whilst *o*-nitrophenylhydrazine reacts readily with *p*-quinones and their monoximes, *p*-nitrophenylhydrazine only reacts readily with the monoximes, and the *m*-compound is oxidised without forming a hydrazone.[73] It is possible that the *o*- and *p*-phenylhydrazine react in the tautomeric *iso*nitro-form, which would be less readily oxidisable. Whilst there is little doubt that the derivatives from quinones are *p*-hydroxyazo-compounds, the monoxime derivatives have different properties. The alternative formulæ are :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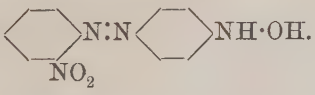

But in their resistance to acids and in their behaviour on oxidation, these compounds do not resemble phenylhydroxylamine derivatives, and they are therefore to be regarded as hydrazones.

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[72] *Trans.*, 1906, **89**, 982.

[73] W. Borsche, *Abstr.*, 1908, i, 66.

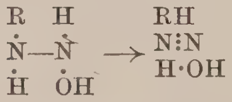
As an appendix to the hydrazones, some experiments on the oxidation of aromatic hydrazines by atmospheric oxygen may be mentioned.[74] The main product is the parent hydrocarbon, according to the equation:

$$R{\cdot}NH{\cdot}NH_2 + O = RH + N_2 + H_2O,$$

but this is always accompanied by some hydrocarbon of the diphenyl series:

$$2R{\cdot}NH{\cdot}NH_2 + O_2 = R{\cdot}R + H_2 + 2N_2 + 2H_2O.$$

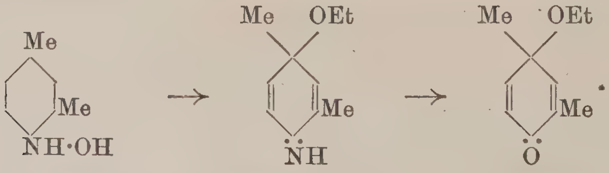
It is suggested that the first product is a hydroxyhydrazine, which then decomposes directly:



$$\begin{array}{cc}R & H\\ \dot{N} — & \dot{N}\\ \dot{H} & \dot{O}H\end{array} \longrightarrow \begin{array}{l}RH\\ N{:}N\\ H{\cdot}OH\end{array}$$

or through the intermediate formation of $R{\cdot}N{:}NH$, to which the transient crimson coloration always observed during the progress of the oxidation may be due.

The remarkable isomeric changes undergone by the arylhydroxylamines in contact with dilute sulphuric acid[75] have been further investigated by Bamberger and his pupils,[76] and considerable light has been thrown on the transformation, although certain points still remain obscure. *m*-Xylylhydroxylamine yields in this way iminoxyloquinol, which readily loses ammonia to form xyloquinol. When alcohol and sulphuric acid are used, water being carefully excluded, the corresponding ethyl imino-ether is obtained, yielding the quinol ether with water:



But the change is not arrested at this point. A part of the substance is transformed into ethers of xylorcinol and xylohydroquinone. It is the mechanism of this reaction that has been studied.

Experimental evidence is produced to show that quinols and their ethers exist in solution as hydrates or alcoholates, and also that water or alcohol may be added on at a $\cdot C{:}C\cdot$ linking. The change of position of OH and OEt may be then only apparent, being due to the addition and removal of water or alcohol at different points on the benzene rings, the only truly isomeric change being the wandering of the methyl group. This is explained as being similar to the pinacone-pinacolin change, which consists in an interchange of methyl and hydroxyl:

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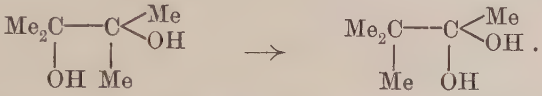
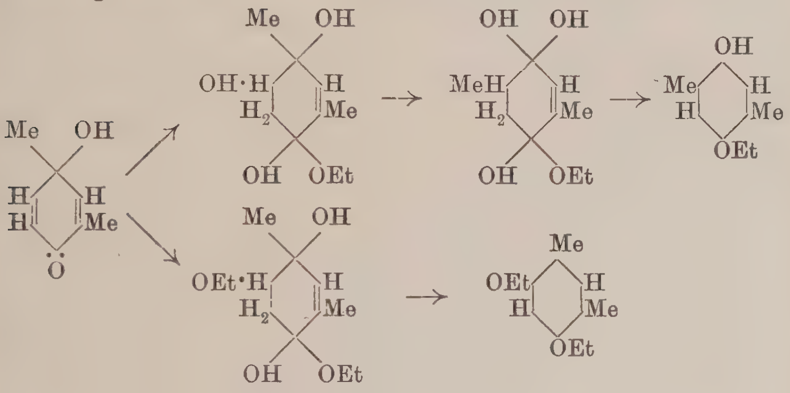
[74] F. D. Chattaway, *Trans.*, 1907, **91**, 1323.

[75] E. Bamberger, *Abstr.*, 1903, i, 83.

[76] *Abstr.*, 1907, i, 516, 517, 518, 519, 520, 521.

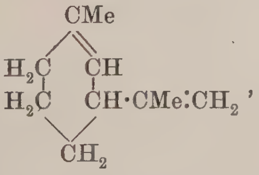


The production of hydroquinone monoethyl ether and xylorcinol diethyl ether from *m*-xyloquinol may then be represented by the following scheme:



The Terpene Group.

The recent work on the terpene group includes several new syntheses from the Manchester laboratories. Thus carvestrene, which is of importance as occupying the same position in the *m*-cymene group as dipentene does in the *p*-cymene series, and to which Baeyer assigned the constitution



has now been synthesised [77] in a manner which fully confirms Baeyer's conclusions. Starting with *cyclo*hexanone-3-carboxylic acid (I) the ethyl ester is caused to react with magnesium methyl iodide, and after hydrolysis and distillation under reduced pressure, the lactone (II) of *cis*-1-methyl-1-*cyclo*hexanol-3-carboxylic acid is obtained:

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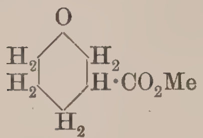
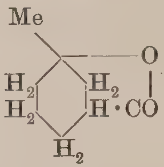
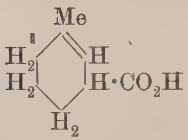
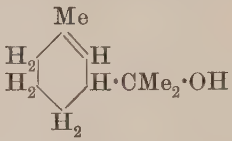
[77] W. H. Perkin, jun., and G. Tattersall, *Trans.*, 1907, 91, 480.


(I.)


(II.)

By the successive action of hydrobromic acid and pyridine, this is converted into the unsaturated 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid (III), the ethyl ester of which reacts with magnesium methyl iodide to form a new alcohol, dihydrocarvestrenol or Δ^1-*m*-menthenol (IV):

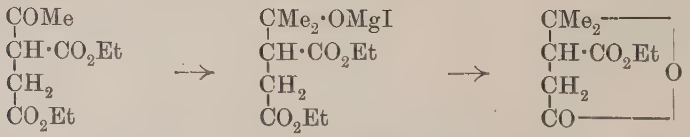

(III.)


(IV.)

This is the meta-analogue of terpineol, and readily yields carvestrene on digestion with potassium hydrogen sulphate. Other interesting products were obtained in the course of the research.

The synthesis of terpin hydrate[78] has now been greatly simplified,[79] it being found that the treatment of ethyl *cyclo*hexanone-4-carboxylate with magnesium methyl iodide, which formed the starting-point of the original process, yields terpin directly under suitable conditions.

Three of the products of the oxidation of pinene, namely, terebic, terpenylic, and homoterpenylic acids, have now been synthesised by a simple application of Grignard's reaction to ketonic esters.[80] Thus ethyl acetosuccinate and magnesium methyl iodide yield ethyl terebate:



In an exactly similar way, ethyl β-acetylglutarate is converted into ethyl terpenylate, and ethyl β-acetyladipate into ethyl homoterpenylate.

Other investigations in the terpene series have been very numerous, and in some cases highly controversial questions of priority occupy a large space in the polemical discussions, a cause of which is the great variety of possible formulæ for certain members of the series.

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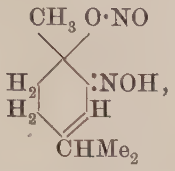
[78] *Ann. Report*, 1904, 117.

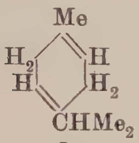
[79] F. W. Kay and W. H. Perkin, jun., *Trans.*, 1907, **91**, 372.

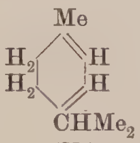
[80] J. L. Simonsen, *ibid.*, 184.

A study of the reactions of terpinene nitrosite has led Wallach[81] to the conclusion that it must be represented by the structural formula



although he does not consider that the compound can be unimolecular, in spite of the results of molecular weight determinations. This accords well with the formula (I) for terpinene suggested by its other chemical reactions and on optical grounds:[82]


(I.)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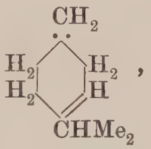
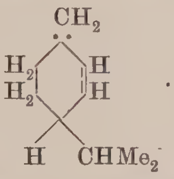

(III.)

although Wallach[83] does not exclude the possibility of (II), and assigns the formula (III) to β-terpinene.

Synthetical phellandrene, from carvomenthene dibromide, resembles the natural hydrocarbon in all respects except its optical activity and boiling point.[84] It is represented by the formula



Dihydrophellandrene and dihydroterpinene are found[85] to be identical with the carvomenthene obtained by reduction of limonene monohydrochloride.

A comparison of various naturally occurring camphenes with the synthetical product has yielded evidence for the existence of two isomeric camphenes.[86]

Nopinone (I), which has hitherto only been obtained in small quantities, is readily prepared by the oxidation of nopic acid, which occurs in the oxidation products of turpentine.[87] When acted on with zinc and ethyl bromoacetate (compare p. 135) a hydroxy-ester is first formed, which on heating with potassium hydrogen sulphate yields the unsaturated ester (II). On distillation, the acid loses carbon dioxide to form β-pinene (III), the configuration of which, however, is not identical with that of the natural hydrocarbon.[88]

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[81] O. Wallach, *Abstr.*, 1907, i, 228.

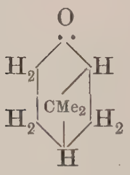
[82] F. W. Semmler, *ibid.*, 714.

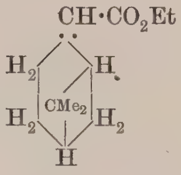
[83] *Abstr.*, 1907, i, 943.

[84] I. L. Kondakoff and I. Schindelmeiser, *ibid.*, 329.

[85] F. W. Semmler, *loc. cit.*

[86] O. Wallach, *Abstr.*, 1907, i, 1061.


(I.)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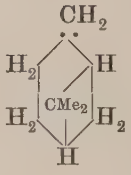
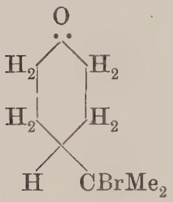
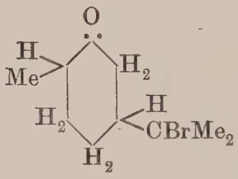

(III.)

An attempt was made[89] to synthesise nopinone by a series of reactions terminating in the production of 4-β-bromo*iso*propyl*cyclo*hexanone (IV), which is related to nopinone (I) in the same way as dihydrocarvone hydrobromide (V) is to carone (VI):


(IV.)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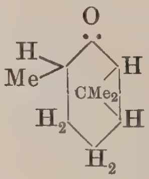
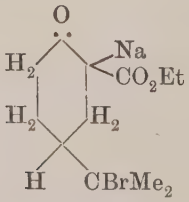
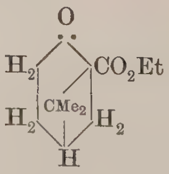

(VI.)

but the ring failed to close under the action of alcoholic potash. An attempt to cause the sodium derivative of ethyl 4-β-bromo*iso*propyl-*cyclo*hexanone-2-carboxylate (VII) to undergo internal condensation with formation of ethyl nopinonecarboxylate (VIII) was


(VII.)


(VIII.)

similarly unsuccessful, from which it appears that, in dicyclic systems, the *cyclo*propane ring is more readily produced than the *cyclo*butane ring.

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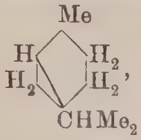
[87] O. Wallach and A. Blumann, *Abstr.*, 1907, i, 936.

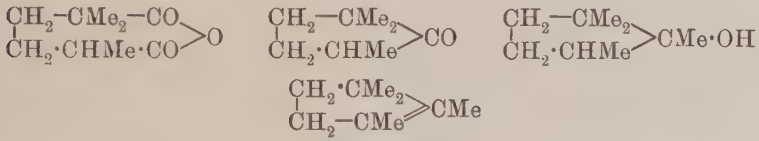
[88] O. Wallach, *ibid.*, 1058.

[89] W. H. Perkin, jun., and J. L. Simonsen, *Trans.*, 1907, **91**, 1736.

Much work has been done on the constitution of sabinene, to which Semmler[90] assigns the formula , special attention having been given to the products obtained on breaking down the ring so as to obtain *cyclo*pentene and *cyclo*pentadiene derivatives. Other investigations have included teresantalic acid[91] and[92] the di- and tri-*cyclo*santalols.



The method adopted for the synthesis of *iso*laurolene[93] has been applied to campholene.[94] $\alpha\alpha\delta$-Trimethyladipic anhydride yields trimethyl*cyclo*pentanone, from which the tertiary alcohol is obtained with magnesium methyl iodide, distillation then yielding campholene :



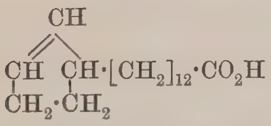
$$\begin{array}{l}CH_2-CMe_2-CO\\ CH_2\cdot CHMe\cdot CO\end{array}>O \qquad \begin{array}{l}CH_2-CMe_2\\ CH_2\cdot CHMe\end{array}>CO \qquad \begin{array}{l}CH_2-CMe_2\\ CH_2\cdot CHMe\end{array}>CMe\cdot OH$$

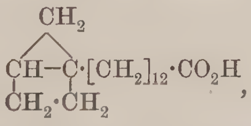
$$\begin{array}{l}CH_2\cdot CMe_2\\ CH_2-CMe\end{array}\geqslant CMe$$

(Campholene.)

The degree of perfection which has been reached by the hypotheses of structural organic chemistry, and their great adaptability to the experimental facts, are perhaps nowhere better illustrated than in the synthetical study of the terpenes, but it has only been possible to mention a few of the very numerous researches in this department of chemistry, and the closely allied group of the camphors must be left unnoticed.

In connexion with the study of natural products, reference should be made to the very careful investigations of chaulmoogric acid[95] and homoeriodictyol.[96] The former is found to be a *cyclo*pentene derivative, and to react in accordance with both of the following formulæ :





but as the acids obtained from the seeds of three botanically distinct species of plants are found to be identical, it is not possible to consider chaulmoogric acid as a mixture of stable isomerides, and tautomerism or dynamic isomerism between the two forms must be assumed. The allied hydnocarpic acid has the same structure, differing only in containing ten methylene groups in the side chain instead of twelve.

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[90] *Abstr.*, 1907, i, 145, 714.

[91] F. W. Semmler and K. Bartelt, *ibid.*, 703, 1062.

[92] F. W. Semmler and K. Bode, *ibid.*, 431.

[93] *Ann. Report*, 1906, 141.

[94] G. Blanc, *Abstr.*, 1907, i, 1058.

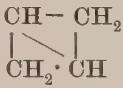
[95] M. Barrowcliff and F. B. Power, *Trans.*, 1907, **91**, 557.

[96] F. B. Power and F. Tutin, *ibid.*, 887.

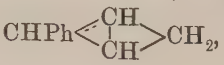
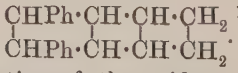
Ring Syntheses and Polycyclic Compounds.

The conditions of stability of hydrocyclic compounds containing three- or four-carbon atom rings have been discussed from various points of view,[97] and it is found that the relative stability is dependent rather on the nature and position of the attached groups than on the number of atoms forming the ring. The reaction between tribromopropane, $CH_2Br\cdot CHBr\cdot CH_2Br$, with ethyl sodiomalonate seemed to offer an equal chance of formation of a *cyclo*propane or *cyclo*butane ring, but the actual course of the reaction was unexpected, unsaturated open-chain compounds being exclusively obtained (see p. 92).

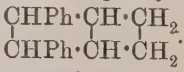
The series of hydrocyclic hydrocarbons has now been completed by the preparation of *cyclo*butane by the reduction of *cyclo*butene with hydrogen and nickel,[98] butane being obtained at a higher temperature. The general chemical behaviour of *cyclo*butene indicates [99] that it is the simplest dicyclic hydrocarbon,

 ,

and this constitution accords with its physical properties, and with the results of the reduction of higher dicyclic hydrocarbons (terpenes) by Sabatier and Senderens' method.

The yellow modification of cinnamylidenemalonic acid, when heated with baryta, yields phenyl*cyclo*butene,  $CHPh<\begin{array}{c}CH\\|\\CH\end{array}>CH_2$, and diphenyl*tricyclo*octane,  $\begin{array}{l}CHPh\cdot CH\cdot CH\cdot CH_2\\ |\qquad\quad |\qquad |\qquad |\\ CHPh\cdot CH\cdot CH\cdot CH_2\end{array}$.[1]

The white modification of the acid, on the other hand, yields the latter hydrocarbon together with diphenyl*dicyclo*hexane:



$$\begin{array}{l}CHPh\cdot CH\cdot CH_2\\ |\qquad\quad |\qquad |\\ CHPh\cdot CH\cdot CH_2\end{array}.$$

Another new *cyclo*butane synthesis is the production, by the action of sulphuric acid on ethyl *s*-dimethylacetonedicarboxylate, of the compound, $\mathrm{CMe}\left<\begin{matrix}\mathrm{CO}\text{——}\\ \mathrm{C(OH)}\end{matrix}\right>\mathrm{CMe\cdot CO_2Et}$, which readily hydrolyses and loses carbon dioxide, yielding the hydroxyketone,

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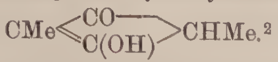
[97] W. H. Perkin, jun., and J. L. Simonsen, *Trans.*, 1907, **91**, 816, 840. See also A. Kötz, *Abstr.*, 1907, i, 1018.

[98] R. Willstätter and J. Bruce, *ibid.*, 1018.

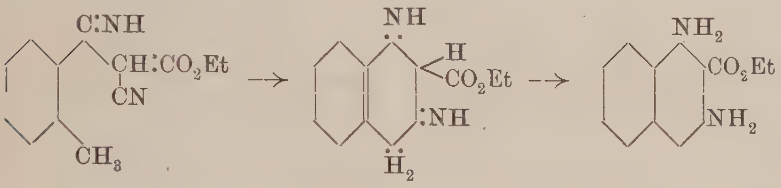
[99] N. Zelinsky and J. Gutt, *ibid.*, 1908, i, 14.

[1] O. Döbner and G. Schmidt, *ibid.*, 1907, i, 204.

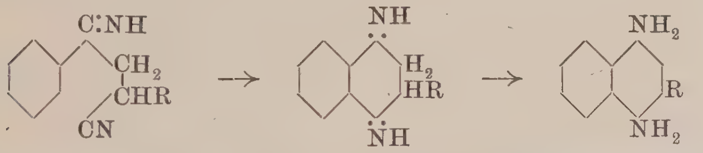


$$\mathrm{CMe}\left<\begin{matrix}\mathrm{CO}\text{——}\\ \mathrm{C(OH)}\end{matrix}\right>\mathrm{CHMe}.$$ [2]

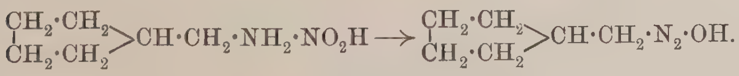
The method of synthesis of naphthylenediamine derivatives described on p. 135 of last year's Report may also be applied when the benzene derivative used has a side-chain of only two carbon atoms, provided that a methyl group occupies the neighbouring position to the side-chain.[3] Thus *o*-toluyl chloride and ethyl sodiocyanoacetate give ethyl cyano-*o*-toluylacetate, $C_6H_4Me\cdot CO\cdot CH(CN)\cdot CO_2Et$, which on heating with ammonium acetate gives ethyl *β*-imino-*α*-cyano-*β*-*o*-tolylpropionate. Acids then convert this into ethyl 1 : 3-naphthylenediamine-2-carboxylate :



1 : 4-Naphthylenediamine derivatives may be synthesised in a similar manner :[4]



Wallach[5] has described a new method of enlarging carbocyclic systems. The cyclic ketones readily condense with esters of bromoacetic acid to form hydroxy-esters, which after treatment with hydrogen bromide and reduction yield cyclylacetic acids. (Cyclyl is suggested as a general designation for univalent cyclic groups.) From the amides of these acids the cyclylmethylamines are obtained by Hofmann's reaction. The nitrites of the cyclylmethylamines are decomposed by acids, the first product being probably an unstable diazo-compound :



$$\left.\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CH_2\cdot NH_2\cdot NO_2H}\longrightarrow\left.\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH\cdot CH_2\cdot N_2\cdot OH}.$$

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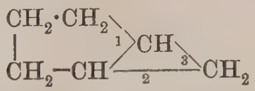
[2] G. Schroeter and C. Stassen, *Abstr.*, 1907, i, 532.

[3] E. F. J. Atkinson, H. Ingham, and J. F. Thorpe, *Trans.*, 1907, **91**, 578.

[4] J. F. Thorpe, *ibid.*, 1004.

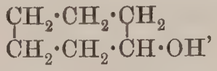
[5] *Abstr.*, 1907, i, 602, 616.

On boiling, nitrogen is removed, and it may be supposed that a dicyclic compound results with loss of water:



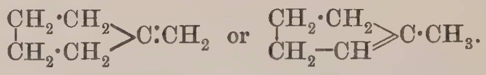
$$\begin{array}{l} CH_2{\cdot}CH_2\diagdown \\ | \qquad\qquad\quad {}^{1}{>}CH\diagdown \\ CH_2{-}CH\diagup\!\!\underset{2}{\text{———}}\!\!{}^{3}\diagdown CH_2 \end{array}$$

If, in the subsequent hydrolysis, the bond 1 is ruptured, an alcohol of the next higher carbocyclic system is obtained:



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}OH, \end{array}$$

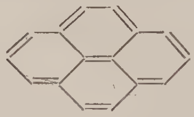
and this is the principal reaction. If, however, rupture takes place at the bonds 2 or 3, which are equivalent, a primary or secondary alcohol is obtained, which may then lose water to form an unsaturated hydrocarbon:

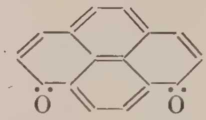


$$\begin{array}{l} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH_2 \end{array}{>}C{:}CH_2 \text{ or } \begin{array}{l} CH_2{\cdot}CH_2 \\ CH_2{-}CH \end{array}{\geqslant}C{\cdot}CH_3.$$

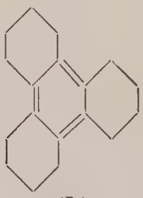
Since the alcohols may be oxidised again to ketones, it is possible in this way to prepare *cyclo*hexanone from *cyclo*pentanone, *cyclo*octanone from suberone, &c.

Of the more complex hydrocarbons with condensed nuclei, an investigation of pyrene[6] has shown that only one of the rings is benzenoid, the others being quinonoid in structure, the arrangement of double linkings in pyrene and pyrenequinone thus being:

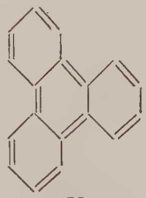




*cyclo*Hexanone and methyl alcohol undergo a condensation[7] with sulphuric acid resembling the formation of mesitylene from acetone, the product being dodecahydrotriphenylene (I), which yields triphenylene (II) on distillation with zinc dust:



(I.)



(II.)

Attention has been called by Collie[8] to the importance, in the building up of rings, of the keten group, $\cdot CH_2 \cdot CO$. Compounds in which multiples of this group are present, of which ethyl acetoacetate and diacetylacetone are simple types, undergo condensation with remarkable readiness. Owing to the labile character of the keten group, such compounds pass, under gentle treatment, with addition or loss of water or carbon dioxide, into the most diverse homocyclic and heterocyclic compounds. Numerous examples of ring-formation under these conditions are adduced in illustration, and the importance of compounds of this type in the synthesis of substances occurring naturally in plants is pointed out. Although the photo-syntheses of the plant have at present no equivalent in the laboratory, it is evident that the study of these labile compounds, many of which undergo condensation even at the ordinary temperature, in presence of feebly acid or alkaline solutions, without the aid of violent condensing agents, may throw considerable light on obscure questions in plant-physiology.

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[6] G. Goldschmiedt, *Abstr.*, 1907, i, 310.

[7] C. Mannich, *ibid.*, 205.

[8] J. N. Collie, *Trans.*, 1907, **91**, 1806. Compare J. N. Collie and E. R. Chrystall, *ibid.*, 1802.

CECIL H. DESCH.

ORGANIC CHEMISTRY—HETEROCYCLIC DIVISION.

In reviewing the chemistry of heterocyclic compounds for the past year, the writer of this Report has been struck chiefly by the large amount of attention given at the present time to compounds occurring naturally or forming essential portions of material obtained from living matter. Besides the important work which is at present being carried on with respect to the fats, the carbohydrates, the fate of the amino-acids[1] in metabolic changes, and the general question of enzyme action, amongst heterocyclic compounds we notice more particularly the work on the fission products of the nucleic acids, which belong to the pyrimidine series, the pyrrole and indole compounds resulting from the hydrolysis of proteins, natural organic dye-stuffs, and more especially the alkaloids.

Other matters of prime importance which are now engaging considerable attention are spacial questions as they affect the formation and stability of rings, and the relationships between the constitution of cyclic compounds and their ability for salt formation, the latter question being intimately bound up with the connexion between colour and constitution, and, one may add, other optical properties such as magnetic rotation.[2]

Spacial Considerations.

Baeyer's strain hypothesis[3] first gave a rational explanation of the observed fact that rings of five or six members were most easily produced, and when formed exhibited the greatest stability; it is therefore a matter of some interest to record observed cases where rings containing less than five or more than six atoms have been produced.

A ring containing one atom each of carbon, nitrogen, and oxygen is supposed by Wieland[4] to exist in the nitrile-oxides, the first of which series was obtained by Werner[5] by removal of hydrogen chloride from benzhydroxamic chloride; since these compounds show no great tendency to form additive products, Wieland replaces the general formula:

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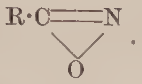
[1] F. Ehrlich, *Abstr.*, 1907, ii, 44.

[2] Compare especially Sir W. H. Perkin, *Trans.*, 1907, **91**, 806.

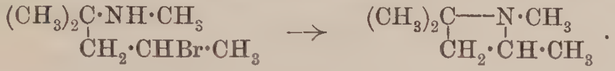
[3] *Ber.*, 1885, **18**, 2277.

[4] *Abstr.*, 1907, i, 527.

[5] *Ibid.*, 1894, i, 585.

R·C:N:O by 

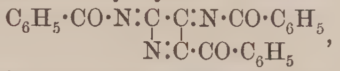
Several four-membered heterocyclic compounds are described. M. Kohn[6] has eliminated hydrogen bromide from δ-bromo-β-methylamino-β-methylpentane hydrobromide and obtained a tertiary saturated base, representing the change in the following manner:



$$\begin{array}{l}(CH_3)_2C\cdot NH\cdot CH_3\\ \quad\quad CH_2\cdot CHBr\cdot CH_3\end{array} \longrightarrow \begin{array}{l}(CH_3)_2C\text{---}N\cdot CH_3\\ \quad\quad CH_2\cdot CH\cdot CH_3\end{array}.$$

The parent substance, trimethyleneimine, was described some years back by Howard and Marckwald.[7]

Diels and Stein[8] regard the termolecular benzoyl cyanide described by Nef[9] as possessing the structure:



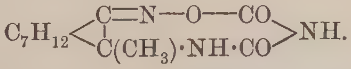
$$\begin{array}{l}C_6H_5\cdot CO\cdot N{:}C\cdot C{:}N\cdot CO\cdot C_6H_5\\ \quad\quad\quad\quad\quad\;\; N{:}C\cdot CO\cdot C_6H_5\end{array},$$

but, on the other hand, W. Meister[10] offers evidence against the ring structure assigned by Dunstan and Goulding to methazonic acid,[11] and considers that it has the open-chain constitution:

$$OH\cdot NO{:}CH\cdot CH{:}N\cdot OH.$$

Blaise and Gault[12] consider that the product obtained from hydrazine and diketopimelic acid contains a seven-membered ring; the writer would suggest that the substance may quite possibly be 1-aminodihydropyridine-2:6-dicarboxylic acid, and a similar criticism may be applicable to the substance obtained by Ciusa[13] by the reduction with sodium and amyl alcohol of the hydrazino-oxime from cinnamylideneacetophenone.

Leach[14] finds that pinene nitrosochloride reacts with two molecules of potassium cyanate, giving a compound $C_{12}H_{17}O_3N_3$, to which he assigns a cyclic structure involving an eight-membered ring:



$$C_7H_{12}<\begin{array}{l}C{=}N\text{—}O\text{—}CO\\ C(CH_3)\cdot NH\cdot CO\end{array}>NH.$$

The formula is based on the fact that the substance exhibits the feebly acidic properties usually associated with an imide, and when reduced by zinc dust and acetic acid gives a very stable ψ-carbamide,

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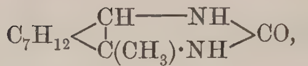
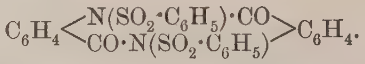
[6] *Abstr.*, 1907, i, 338.
[7] *Ibid.*, 1899, i, 749.
[8] *Ibid.*, 1907, i, 528.
[9] *Ibid.*, 1896, i, 71.
[10] *Ibid.*, 1907, i, 885.
[11] *Trans.*, 1900, **77**, 1262.
[12] *Abstr.*, 1907, i, 280.
[13] *Ibid.*, 62.
[14] *Trans.*, 1907, **91**, 10.



$$C_7H_{12}<\begin{array}{l}CH\text{——}NH\\ C(CH_3)\cdot NH\end{array}>CO$$

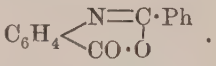
$C_7H_{12}<\begin{array}{l}CH\text{——}NH\\ C(CH_3)\cdot NH\end{array}>CO$, whilst cyanic acid is liberated as carbon dioxide and ammonia.

Schroeter[15] in preparing benzenesulphonylanthranilic acid has observed a by-product insoluble in alkalis and evidently a bimolecular anhydride of the constitution:



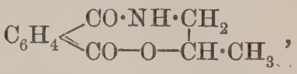
$$C_6H_4<\begin{array}{l}N(SO_2\cdot C_6H_5)\cdot CO\\ CO\cdot N(SO_2\cdot C_6H_5)\end{array}>C_6H_4.$$

Whilst an eight-membered ring is involved in this case, Schroeter considers that the unimolecular "acylanthranils" obtained in many cases during the acylation of anthranilic acid are metoxazones of the type:



$$C_6H_4<\begin{array}{l}N{=}C\cdot Ph\\ CO\cdot O\end{array}.$$

Gabriel assumed[16] the intermediate formation of a nine-membered ring in the transformation of γ-bromopropylphthalimide into γ-hydroxypropylphthalimide, and, in carrying out corresponding reactions with β-bromopropylphthalimide, Bartholdy[17] has succeeded in actually isolating the corresponding compound:

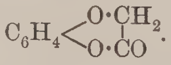


$$C_6H_4<\begin{array}{l}CO\cdot NH\cdot CH_2\\ CO{-}O{-}CH\cdot CH_3\end{array},$$

containing an eight-membered ring.

Spallino's[18] assumption that the internal anhydride, $C_{15}H_9O_3N$, obtained from phthalonic acid and anthranilic acid contains a nine-membered ring has some justification from the results of analyses and the molecular weight determination.

Bischoff and E. Fröhlich[19] have examined the action of halogenised acetylhalides on the sodium salts of dihydric phenols in the hope of obtaining lactones of the formula:



$$C_6H_4<\begin{array}{l}O\cdot CH_2\\ O\cdot CO\end{array}.$$

Whilst positive results were obtained in the case of catechol, resorcinol and quinol did not give compounds of the desired type; although it is possible that a two-fold polymeride is formed in the case of resorcinol, such a compound would involve a fourteen-membered ring.

When one comes to the question of actually realising any given cyclic formula, one needs to know the conditions under which ring

[15] *Abstr.*, 1907, i, 529.

[16] *Ibid.*, 1905, i, 649.

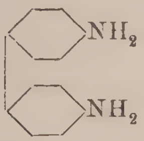
[17] *Ibid.*, 1907, i, 1043.

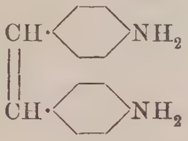
[18] *Ibid.*, 872.

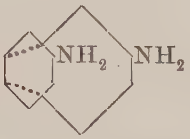
[19] *Ibid.*, 696, 697.

closing is possible. There are evidently other factors at work besides those indicated in Baeyer's original strain theory. Where a portion of the new cyclic structure is built up with two ortho-carbon atoms of an aromatic nucleus, there is the possibility of building a larger ring than if one starts with two carbon atoms of aliphatic function. This point is drawn attention to by J. v. Braun,[20] who finds that *o*-aminophenylbutyric acid cannot be isolated in the free condition, but when liberated from its salts passes immediately into an ε-lactam, the ring homologue of oxindol and hydrocarbostyril.

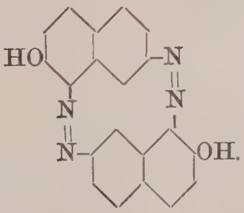
Kaufler [21] introduces a somewhat novel conception in supposing that, where a substance contains two aromatic nuclei in its molecule, these are frequently inclined towards one another, so bringing reactive groups into sufficient proximity to make ring formation possible. The following formulæ:







are assigned to benzidine, *p*-diaminostilbene, and 2 : 7-naphthylenediamine respectively, and may account for the fact that the first gives an azimide according to Vaubel and Scheuer [22] and a unimolecular phthalylbenzidine,[23] whilst a unimolecular phthalyl derivative may be obtained from 2 : 7-naphthylenediamine, which is insoluble both in acids and alkalis. Kaufler and Karrer also find that, when 7-amino-2-naphthol is diazotised, the diazonium salt couples with itself to a bimolecular compound, which is probably



But special conditions may prevent ring formation by what is usually known as "steric hindrance," and so Scholtz and Wassermann [24] in continuation of earlier work find that, whilst arylamines and αε-dibromopentane usually give *N*-arylated piperidines, the same result cannot be obtained with *o*-toluidine or α-naphthylamine. A somewhat similar case of steric hindrance has been observed by Jürgens.[25]

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[20] *Abstr.*, 1907, i, 524.

[21] *Ibid.*, 307, 776, 794, 795, 799.

[22] *Ibid.*, 1906, i, 323. The mol. wt. is unknown.

[23] Koller, *ibid.*, 1904, i, 778.

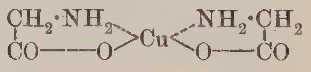
[24] *Abstr.*, 1907, i, 339.

Willstätter's researches on aniline-black have induced Bucherer[26] to bring all syntheses of indamines and azines by the oxidation of mono- or di-amines under one common point of view. A diamine (ortho or para) is oxidised to a di-imide, and this will unite with a compound which may be represented by HR, giving a second diamine differing from that originally employed by having one of its hydrogen atoms replaced by the group R. The process can then be repeated, and even the synthesis of such a complex compound as safranine can be quite easily brought into the scheme.

Methods for opening rings also deserve notice, and J. v. Braun[27] finds that, in addition to the treatment of benzoyl derivatives of cyclic secondary amines with phosphorus pentahalides, cyanogen bromide frequently gives satisfactory results, Thus the reagent unites with 1-phenylpiperidine, giving phenyl-ω-bromoamylcyanamide, which can afterwards be hydrolysed to the bromoamylaniline.

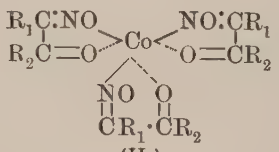
The part played by the "keten" group, $CH_2\cdot CO$, in the synthesis of a large number of compounds of entirely different series, some open-chain, some homocyclic, others heterocyclic, occurring in nature has been discussed by Collie.[28]

The application of heterocyclic structure to the compounds formed by many metals with amino-acids, Werner's co-ordination number being employed, is due in the first place to Ley,[29] and has been enthusiastically adopted by Tschugaeff.[30] In this scheme, copper glycine is represented as (I):



$$\begin{array}{l}CH_2\cdot NH_2\\ |\\ CO---O\end{array}\!\!>Cu<\!\!\begin{array}{r}NH_2\cdot CH_2\\ |\\ O---CO\end{array}$$

(I.)



(II.)

and Tschugaeff extends the idea to certain compounds of cobalt, its derivatives with the oximes of α-diketones (for example, nitroso-β-naphthol) being represented by the general formula (II). A matter affecting heterocyclic compounds in general is discussed by Brühl,[31] who shows that, whilst the molecular refraction and dispersion of saturated heterocyclic compounds are normal (that is, correspond with the values reckoned in the ordinary manner), the values obtained for unsaturated heterocyclic compounds point to optical depression.

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[25] *Abstr.*, 1907, i, 1036.

[26] *Ibid.*, 981.

[27] *Ibid.*, 960. Compare *ibid.*, 1900, i, 430.

[28] *Trans.*, 1907, **91**, 1806.

[29] *Abstr.*, 1905, i, 175.

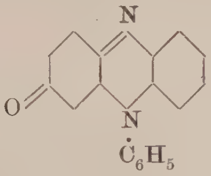
[30] *Ibid.*, 1907, i, 392, 830.

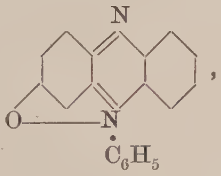
[31] *Trans.*, 1907, **91**, 115.

"*Onium*" *Salts and Pseudo-bases.*

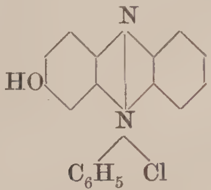
The relationships existing between cyclic ammonium, thionium, and oxonium salts and the pseudo- (carbinol) bases obtained from them have once more attracted considerable attention. It is now a well-recognised fact that in those cases where the carbinol group (or oximido-group in case of azines) is in the para-position to a hydroxyl or amino-group, water is removed with greater or less ease, in fact, in the case of azines such removal of the elements of water is spontaneous, and the hydroxylated azonium salts are hydrolytically dissociated.

Thus whilst safranine and aposafranine salts are derived from powerful bases, the corresponding hydroxylated azonium salts are characterised by extreme instability, and pass spontaneously on treatment with water by loss of acid into aposafranone or hydroxyaposafranone. For aposafranone, two formulæ have been proposed, the para-quinonoid and the ortho-quinonoid:

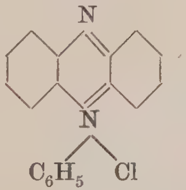




either of which would correspond with the salt:



or



The second formula representing aposafranone as an internal salt of the phenolic and quaternary ammonium functions is due to Kehrmann, and is in many respects at variance with the properties exhibited by the substance, for one would expect such a compound to add on the elements of water and give a strongly basic ammonium hydroxide. This, as we have seen, is not the case, any more than it is with the similarly constituted substances derived from dihydroxyphenylacridine. An example in the latter series is given by A. E. Dunstan and Miss Cleaverley,[32] who have obtained 2:8-dihydroxy-5-phenyl-3:7-dimethylacridine from the commercial dye-stuff, benzoflavine, by heating the base under pressure with diluted sulphuric acid. The hydroxyl groups were acetylated, methyl iodide then added, and the resulting quaternary ammonium salt hydrolysed. When alkali is added to a salt of the dihydroxyacridinium compound (I), a carbinol base does not separate (II), but in its place the corresponding anhydro-compound (III):

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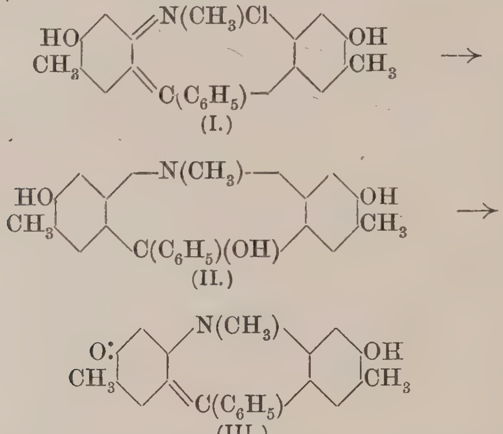
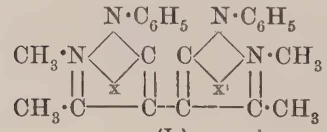
[32] *Trans.*, 1907, **91**, 1619.

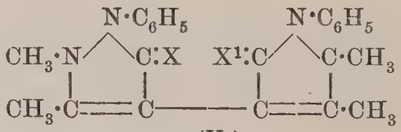

(I.)

(II.)

(III.)

Considerations of this character make one somewhat critical as to whether the pyrines obtained by A. Michaelis, Rademacher, and Schmiedekampf[33] from bis-1-phenyl-3-methyl-5-pyrazolone are really to be represented structurally as the authors do by formula (I) and not rather by formula (II):


(I.)


(II.)

They are obtained by acting on the corresponding bis-quaternary ammonium compounds with alkalis, hydrogen (or other) sulphide, primary bases, &c., so that X and X^1, which may be the same, or different, are either O, S, Se, NH, $N\cdot C_6H_5$, &c. In fact, Michaelis and Hillmann[34] themselves prefer the formula of an ammonium hydroxide (I) to that of a bridged-ring compound (II) for the product of the action of aniline on 4-chloro-2 : 6-lutidine methochloride:

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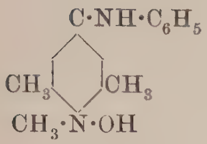
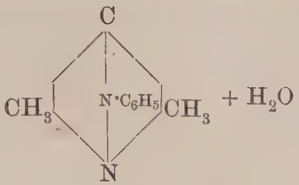
[33] *Abstr.*, 1907, i, 731.

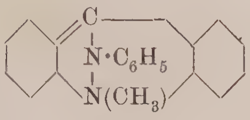
[34] *Ibid.*, 726.



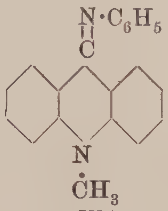
(I.)



(II.)



(III.)

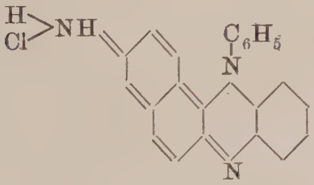


[35]

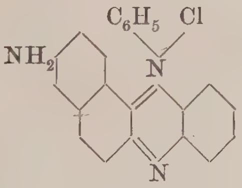
(IV.)

although formula (III) is accepted for the product from aniline and 5-chloroacridine methochloride when (IV) is available.

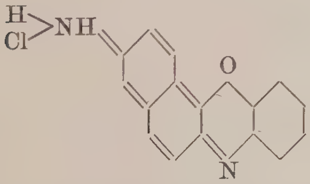
Kehrmann[36] seems, however, prepared to admit the possibility of para-quinonoid structure in some cases. The condensation product from 6-amino-1 : 2-naphthaquinone and *o*-aminodiphenylamine differs so markedly from its isomerides in its properties that, in view of the isolation of 2 : 6-naphthaquinone by Willstätter and Parnas,[37] Kehrmann is quite inclined to admit the substance having the formula (I) instead of (II):



(I.)



(II.)



(III.)

whilst formula (III) is suggested for the oxazine from 6-amino-1 : 2-naphthaquinone and *o*-aminophenol on account of its resemblance to Meldola's blue.

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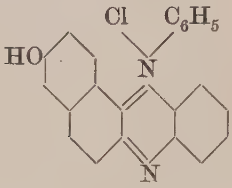
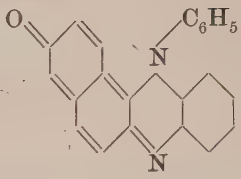
[35] *Ann. Report*, 1906, 157.

[36] *Abstr.*, 1907, i, 563.

[37] *Ibid.*, 425.

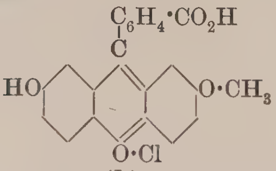
Corresponding compounds are obtained with 6-hydroxy-1 : 2-naphthaquinone; the 7-hydroxyphenyl*iso*naphthaphenazonium salts are orange-red, but the anhydro-base is dark blue, and the relationship can be expressed by the formulæ:



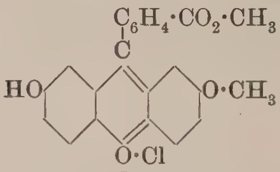


It may be noted that a very similar constitution (derived from a 1 : 7-naphthaquinone) was suggested in last year's Report[38] for a dark blue anhydro-base derived from phenonaphthacridine.

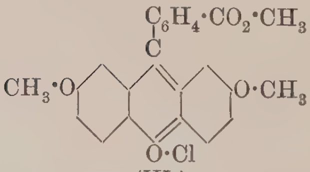
One of the most interesting contributions of the past year to the constitution of oxonium salts is the work of A. G. Green and King[39] on the halide salts of the quinonoid esters of phenol- and quinolphthaleins. In addition to the isolation of the free quinonoid monomethyl ester of phenolphthalein from the hydrochloride mentioned in last year's Report,[40] the new compounds derived from quinolphthalein, represented by formulæ (I), (II), and (III), have been prepared and examined:



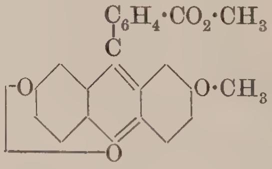
(I.)



(II.)



(III.)



(IV.)

The free base corresponding to the second formula is represented by the authors as possessing structure (IV), but from their paper it seems doubtful if it has been isolated, since whilst the chloride itself is soluble in water with an orange-red colour, it does not dissolve in aqueous alkalis, and if warmed with them hydrolyses, forming the original lactoid monomethyl ether from which it was produced with methyl alcohol and hydrogen chloride.

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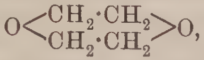
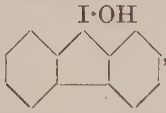
[38] *Ann. Report*, 1906, 172.

[39] *Abstr.*, 1907, i, 933.

[40] *Ann. Report*, 1906, 179.

Another very important paper on phenopyrylium compounds is due to Decker and von Fellenberg,[41] in which a large number of substances, the oxygen analogues of quaternary quinolinium and acridinium compounds, are described. The coeroxonium and coerthionium compounds are further studied,[42] and the theory connected with the conjugate double linkings in application of Thiele's theory undergoes further extension.

A few more papers on oxonium salts may be mentioned: Hantzsch and Denstorff[43] and Feist[44] continue the discussion on the hydroperbromides of negatively substituted pyrones, whilst Faworsky[45] finds that ethylene ether,  $O<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>O$, readily forms oxonium salts. Finally, we may note that a cyclic, basic iodonium compound, diphenyleneiodonium hydroxide,  has been prepared by Mascarelli[46] by the action of moist silver oxide on di-iodoxy- or di-iodoso-diphenyl; its acetate and oxalate are described.

Five-membered Rings.

Amongst syntheses of pyrrole derivatives may be noted Clarke and Lapworth's[47] production of Smith's tetraphenylpyrrole[48] by the action of heat on γ-cyano-α-benzoyl-γ-anilino-$\beta\gamma$-diphenylpropane, and the preparation of several pyrroles of high molecular weight by J. Schmidt and R. Schall,[49] who have employed aminodiphenyl derivatives in conjunction with acetonylacetone. Ethyl phenacylacetate condenses readily with the three nitroanilines to give the esters of the 5-phenyl-1-nitrophenyl-2-methylpyrrole-3-carboxylic acids, Borsche and Titsingh[50] observing no steric hindrance even with *o*-nitroaniline, although it is incapable of giving piperazine derivatives when heated with ethylene dibromide and sodium acetate to 150°.

Pyrrolidone, being now easily obtained by the electrolytic reduction of succinimide,[51] has been further studied by Tafel and Wassmuth,[52] whilst the thiopyrrolidone, obtained from it by means of phosphorus pentasulphide, is found by Tafel and Lawaczeck[53] to give a strong base on methylation, the methyl group becoming attached to the sulphur atoms.

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[41] *Abstr.*, 1907, i, 950, 1064.

[42] *Ann. Report*, 1906, 153.

[43] *Abstr.*, 1907, i, 233.

[44] *Ibid.*, 949.

[45] *Ibid.*, 274.

[46] *Ibid.*, 1021.

[47] *Trans.*, 1907, **91**, 704.

[48] *Ibid.*, 1890, **57**, 646.

[49] *Abstr.*, 1907, i, 724.

[50] *Ibid.*, 1908, i, 103.

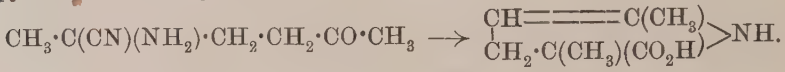
[51] *Abstr.*, 1900, i, 557.

[52] *Ibid.*, 1907, i, 719.

[53] *Ibid.*, 720.

L 2

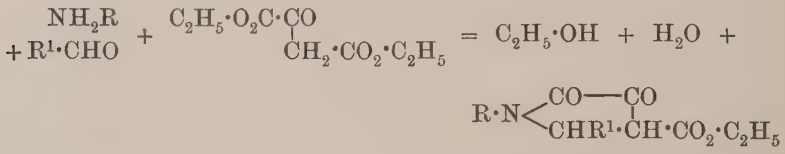
Other pyrrolidone syntheses have been effected by H. Weber,[54] whilst Zelinsky and Schlesinger[55] have condensed acetonylacetone, ammonium chloride, and potassium cyanide to an amino-nitrile, which, when heated with hydrochloric acid, passes over into 2 : 5-dimethylpyrroline-5-carboxylic acid :



$$CH_3\cdot C(CN)(NH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow \left.\begin{array}{l} CH{=\!=\!=\!=}C(CH_3) \\ CH_2\cdot C(CH_3)(CO_2H) \end{array}\right\rangle NH.$$

Markwalder[56] finds that methyl γ-anilinopropyl ketone gives the hydrobromide of 1-phenyl-2-methyl-4 : 5-dihydropyrrole when treated with hydrochloric acid, but on attempting to liberate the base the anilino-ketone is regenerated.

In addition to the synthesis by Emmert[57] of 1-phenyl-5-methylpyrrolidines by simultaneous electrolytic reduction of lævulic acid and nitrobenzene, a general reaction discovered by L. J. Simon and Conduché[58] is of interest, aldehydes readily condensing with ethyl oxalacetate in presence of ammonia or primary amines to give 2 : 3-diketopyrrolidinecarboxylic esters :



$$\begin{array}{l} NH_2R \\ +R^1\cdot CHO \end{array} + \begin{array}{l} C_2H_5\cdot O_2C\cdot CO \\ \qquad\qquad CH_2\cdot CO_2\cdot C_2H_5 \end{array} = C_2H_5\cdot OH + H_2O + R\cdot N\left\langle\begin{array}{l} CO{-\!-}CO \\ CHR^1\cdot CH\cdot CO_2\cdot C_2H_5 \end{array}\right.$$

Several interesting reactions of pyrrole and its derivatives have been studied, Pictet and Rilliet[59] finding that pyrrole and formaldehyde yield under suitable conditions a solid product, $C_{11}H_{12}ON_2$, which, when distilled, gives some α-methylpyrrole, but on distillation with zinc dust furnishes α-picoline. Further, when methylene chloride is heated to 120—130° with potassium pyrrole, two dipyridylmethanes are produced, one, melting at 112°, is evidently linked by the nitrogen atoms, as it will not react with potassium, whilst the other, melting at 66°, is probably a transformation product of the first compound and linked by carbon in the α-position, as it reacts vigorously with potassium. The hope that either of these might furnish pyridylpyrrole on passage through a red-hot tube and so lead to another synthesis of nicotine was not realised.

Pyrrole compounds, in which the hydrogen of the imino-group is replaced by hydroxyl or an amino-group, behave frequently in an interesting manner. Angeli and Marchetti[60] consider that the nitroso-derivative they have obtained from 1-hydroxy-2 : 5-dimethyl pyrrole probably possesses the second of the two formulæ:

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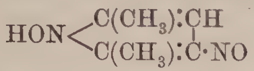
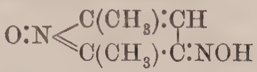
[54] *Abstr.*, 1900, i, 1071.
[55] *Ibid.*, 720.
[56] *Ibid.*, 1907, i, 639.
[57] *Ibid.*, 339.
[58] *Ibid.*, 963.
[59] *Ibid.*, 445.
[60] *Ibid.*, 1907, i, 436.



$$HON<\begin{array}{l}C(CH_3){:}CH\\C(CH_3){:}C\cdot NO\end{array}$$



$$O{:}N<\begin{array}{l}C(CH_3){:}CH\\C(CH_3)\cdot C{:}NOH\end{array}$$

for, when hydrolysed in presence of hydroxylamine, it yields the trioxime of hexane-2 : 3 : 5-trione,

$$CH_3\cdot C({:}NOH)\cdot C({:}NOH)\cdot CH_2\cdot C({:}NOH)\cdot CH_3.$$

Bülow and Klemann[61] have examined the action of nitrous acid on amino-compounds in a number of cases, and find that, whilst the amino-group is diazotised when attached to carbon, be the compound carbocyclic or heterocyclic, amino-groups attached to nitrogen in a ring are removed in the form of nitrous oxide:

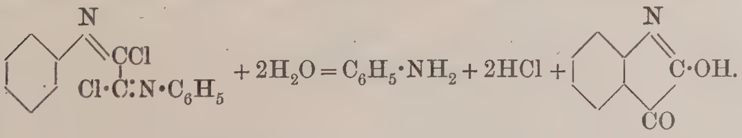
$$>N\cdot NH_2 + HNO_2 = H_2O + N_2O + >NH.$$

The reaction is of considerable importance, as we shall see in the case of the *N*-aminotriazoles.

The occurrence of pyrrole groupings in various proteins is now well recognised, and papers on chlorophyll have appeared by Koźniewski and Marchlewski,[62] and Willstätter, in conjunction with Hocheder,[63] and Mieg.[64] Willstätter and Hocheder have isolated and characterised several hydrolytic products from chlorophyll, most of which contain nitrogen; they also isolated phytol, $C_{20}H_{40}O$, a thick, oily, unsaturated primary alcohol boiling at 145° under a pressure of 0·03—0·04 mm.

Küster[65] has oxidised the "acid" and "basic" hæmopyrroles, and finds that both of them give methyl ethylmaleinimide on oxidation. The hæmopyrrole of weak acid function is the one most easily, oxidised, and it is probably 3-methyl-4-ethylpyrrole, whilst the other "basic" hæmopyrrole is either 3-methyl-4-ethylpyrroline or perhaps 2 : 4-dimethyl-3-ethylpyrroline, one of the methyl groups being lost in the oxidation.

Carrasco and Padoa[66] find that 1-methylindole may be produced from dimethyl-*o*-toluidine by passing it over reduced nickel at 300° to 330°, whilst the following syntheses lead to isatin and its derivatives. Rudolf Bauer[67] finds that if oxanilide be treated with phosphorus pentachloride, diphenyloxalimino-chloride is formed, which if heated on the water-bath and poured into water furnishes isatin:



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[61] *Abstr.*, 1908, i, 54.

[62] *Ibid.*, 1907, i, 866.

[63] *Ibid.*, 784.

[64] *Ibid.*, 865.

[65] *Ibid.*, 572.

[66] *Ibid.*, 152.

[67] *Ibid.*, 603.

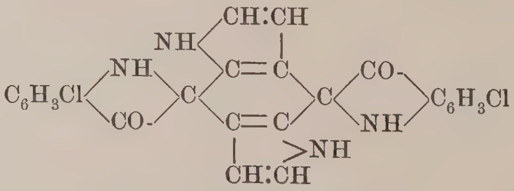
The reaction, discovered by P. J. Meyer,[68] of producing *p*-tolly-*p*-methylimesatin by the action of dichloroacetic acid on *p*-toluidine has been examined by Ostromisslensky.[69] In trying the reaction with aniline, Heller[70] obtained a substance to which he assigned the constitution of a diaminostilbenedicarboxylic acid, but the present author finds that a portion of the reaction product (about 24 per cent.) does consist of phenylimesatin.

W. Peters[71] finds that many of the metallic derivatives of isatin are nitrogen derivatives, and the sodium oxygen salt could not be isolated, and Deussen, G. Heller, and Nötzel[72] have followed the gradual change of sodium *N*-isatin to sodium isatate, and of the latter back to isatin under the influence of hydrochloric acid by conductivity determinations.

Heller[73] has further followed the colour changes of these compounds, and observes that sodium *N*-isatin dissolves in water with the same violet-red shade that isatin gives at first in dilute alkali; the change to yellow is due to the formation of sodium isatate, but the *aci*-isatin salt is probably formed intermediately; the silver derivative certainly behaves as an oxygen salt and gives an *O*-ether[74] with methyl iodide, whilst the sodium derivative furnishes *N*-methylisatin.

This *O*-ether is very reactive, giving a stable dianil with aniline and α-isatinphenylhydrazone with phenylhydrazine, the latter being identical with Baeyer's benzeneazoindoxyl.[75] The latter substance by reduction and subsequent oxidation passes into indigo.

Condensation products of isatin have been studied by C. Liebermann and R. Krauss[76] and C. Haslinger.[77] In the former papers, the indigo-like colouring matters, of which indophenine, pyrrole-blue, and isatin-blue may be taken as typical, are submitted to a lengthy examination, and in some cases provisional formulæ are assigned; three such formulæ may be given here:



Dichloropyrrole-blue B.

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[68] *Ber.*, 1883, **16**, 925, 926, 2261.

[69] *Ibid.*, 1907, **40**, 4972.

[70] *Abstr.*, 1904, i, 730.

[71] *Ibid.*, 1907, i, 239.

[72] *Ibid.*, 442.

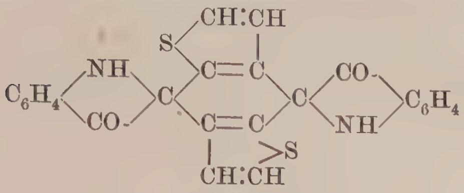
[73] *Ibid.*, 442.

[74] Baeyer and Oeconomides, *Abstr.*, 1883, 201.

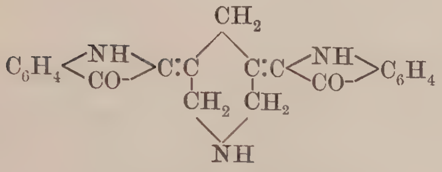
[75] *Abstr.*, 1884, 74.

[76] *Ibid.*, 1907, i, 657.

[77] *Ibid.*, 975.

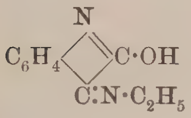


Indophenine.

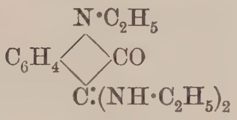


Blue from isatindipiperidide.[78]

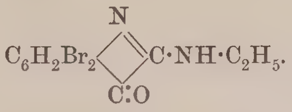
C. Liebermann and Danaila[79] have also oxidised the phenolisatins, whilst Haslinger has examined the action of ethylamine on isatin and its derivatives. He finds that three classes of derivatives may be produced, of which the following may be taken as typical:



Yellow.



Colourless.

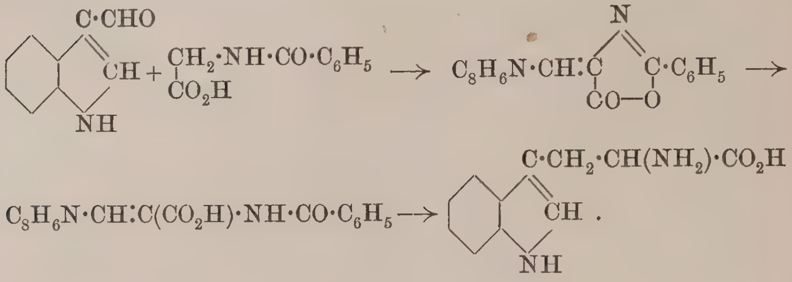


Green.

An indole derivative which has aroused considerable interest in the last few years is tryptophan, a product of the hydrolysis of many proteins. Neuberg and Popowsky[80] have worked out a method for obtaining the substance from fibrin, and prepared and analysed several coloured halogen derivatives, whilst Abderhalden and Kempe[81] have prepared several polypeptides from tryptophan, incidentally discovering that the violet coloration with bromine or chlorine water is peculiar to tryptophan itself, since the reaction is not given by its polypeptides until after pancreatic digestion.

Finally, the synthesis of racemic tryptophan has been effected by Ellinger and Flamand.[82] Indole-aldehyde and benzoylglycine condense to an azlactone, which hydrolyses to α-benzoylaminoindolylacrylic acid. The latter compound by reduction and hydrolysis gives tryptophan:

[78] Schotten, *Abstr.*, 1891, 928, 1491.
[79] *Abstr.*, 1907, i, 976.
[80] *Ibid.*, 253.
[81] *Ibid.*, 652.
[82] *Ibid.*, 727.



M. Freund and Wirsing[83] have described di-*p*-dimethylaminoindigotin; they start with *p*-aminodimethylaniline, convert this into dimethylaminophenylglycine, fuse with sodamide, dissolve the product in water, and oxidise. The substance is easily soluble in organic solvents with a green colour, and dyes wool a light green shade from an acetic acid solution. The solution in hydrochloric and sulphuric acids is blue, but will not dye wool.

A. G. Perkin and Bloxam[84] have investigated the constituents of natural indigo, and find that indigo-brown contains at least three constituents, to which the formulæ $C_{16}H_{12}O_3N_2$, $C_{16}H_{14}O_4N_2$, and $C_{24}H_{22}O_5N_3$ are assigned. They are probably complex indoxyl derivatives, since they yield anthranilic acid when digested with 50 per cent. potash solution. Besides these substances, A. G. Perkin has isolated a rhamnoside of kaempferol,[85] $C_{27}H_{30}O_{14}$, from the indigo of *Indigofera arrecta*, but it is improbable that the kaempferol is identical with the "Indigo-yellow" obtained by Bolley and Crinsoz[86] from Bengal indigo.

A. G. Perkin and Bloxam[87] have so improved the method of isolating indican, $C_{14}H_{17}O_6N,3H_2O$, from indigo leaves by extraction with acetone that they can obtain more than 30 grams per kilo. Dextrose is obtained by hydrolysis, but by carrying out this operation with hot dilute sulphuric acid the indoxyl is converted into a brown substance; nevertheless, its estimation has been effected by conversion into indirubin by isatin. This is the basis of a quantitative process for indoxyl devised by Orchardson, Wood, and Bloxam.[88]

Closely connected with indigo is the sulphur analogue, thioindigo, which is obtained from carboxyphenylthioglycollic acid. P. Friedländer and Chwala describe methods for obtaining arylthioglycollic acids;[89] it may be noted that the amino-compounds are not

[83] *Abstr.*, 1907, i, 254.

[84] *Trans.*, 1907, **91**, 279.

[85] *Ibid.*, 435.

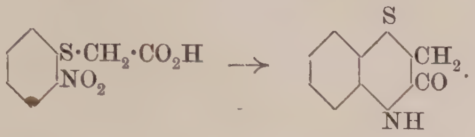
[86] *Jahresb.*, 1866, 573.

[87] *Trans.*, 1907, **91**, 1715.

[88] *Abstr.*, 1907, ii, 203.

[89] *Abstr.*, 1907, i. 525.

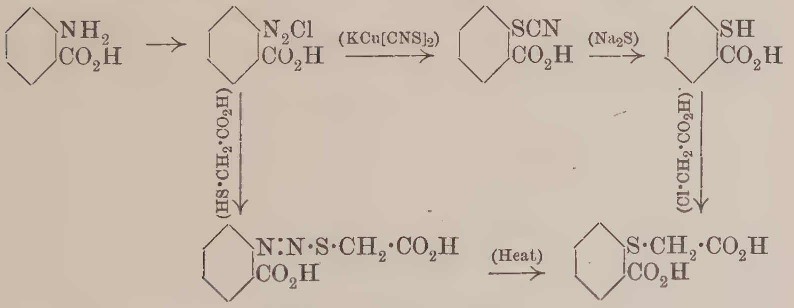
obtained from the nitro-derivatives by reduction, since ring formation occurs :



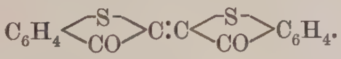
The so-called thionaphthen derivatives form the subject of an important paper by Friedländer.[90]

Thionaphthen, $C_6H_4{<}\genfrac{}{}{0pt}{}{CH}{S}{>}CH$, has been described by Gattermann and Lockhart and by Komppa ; it shows the greatest analogy to naphthalene. The hydroxylic derivative, $C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)}{S}{>}CH$, resembles α-naphthol in odour ; it is volatile with steam, and the methyl ethers of the two substances smell alike and have nearly the same boiling point. The *O*-carboxylic acids are equally unstable, and the azo-derivatives have the same shade. Similar resemblances are observed for the amino-compounds.

Two methods for passing from anthranilic acid to carboxyphenylthioglycollic acid can be represented by the following scheme :



When the carboxyphenylthioglycollic acid is heated with sodium hydroxide to 150—160°, it passes into sodium hydroxythionaphthencarboxylate (analogue of indoxylcarboxylic acid), the aqueous solution of which is readily oxidised to thioindigo :



$$C_6H_4{<}\genfrac{}{}{0pt}{}{S}{CO}{>}C{:}C{<}\genfrac{}{}{0pt}{}{S}{CO}{>}C_6H_4.$$

From *o*-aminothiophenol, *o*-cyanophenylthioglycollic acid may be prepared, which isomerises when warmed with dilute alkali to aminothionaphthencarboxylic acid ; from the latter compound, carbon dioxide may be removed by boiling with water, and the analogue of α-naphthylamine produced.

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[90] *Abstr.*, 1907, i, 334.

Respecting indigo and thioindigo, Falk and Nelson[91] speculate on the stereochemistry of these substances, and think it likely that, whilst indigo is a *cis*-compound, its diacetyl derivative as well as thioindigo belongs to the *trans*-series.

Other work on complex derivatives containing the pyrrole nucleus may be briefly mentioned, new carbazole derivatives having been prepared by Borsche and Feise,[92] J. Schmidt and R. Schall,[93] and G. Schultz and Hauenstein,[94] whilst Fichter and Probst have continued the work on quindoline derivatives.[95]

Pyrazoles and Iminazoles.

Pyrazole derivatives have been prepared by Bülow and Deseniss,[96] Stoermer,[97] Franz Sachs and Alsleben,[98] A. Michaelis with Mielecke,[99] and Klopstock,[1] whilst the formation of ethyl 1-phenylpyrazole-3-acetate-4-carboxylate and ethyl 1-phenylpyrazole-4-carboxylate observed by W. Wislicenus and Breit[2] in the condensation of ethyl formylglutaconate with phenylhydrazine is notable in that the production of the latter ester involves the scission of ethyl acetate (as such) from the molecule.

Pellizzari and Roncagliolo[3] have examined the condensation products of aminocarbocarbazide,[4] $NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2$, finding that it loses ammonia on heating, giving urazine (see triazoles), whilst it condenses as a primary hydrazine with acetylacetone to give a derivative of dimethylpyrazole. Ethyl ethoxymethylenemalonate has been employed by A. Michaelis and Remy[5] in the synthesis of pyrazolones; A. R. Smith and J. F. Thorpe obtain 4-cyano-1-phenyl-3-benzyl-4-ethylpyrazolone from phenylhydrazine and the ethyl derivatives of ethyl α-cyano-γ-phenylacetoacetate,[6] and Ruhemann[7] has prepared monomethyl 1-phenyl-5-pyrazolonedicarboxylate, starting with the methyl dicarboxyaconitate of Anschütz.

Pyrazolonimines have been prepared by Moureu and Lazennec,[8] who condense acetylenic or β-ketonic nitriles[9] with hydrazines; where the latter reagents are replaced by hydroxylamine, *iso*oxazolones result.

In addition to other pyrazolone syntheses by Michaelis[10] and Schenk,[11]

[91] *Abstr.*, 1908, i, 107.

[92] *Ibid.*, 1907, i, 242.

[93] *Ibid.*, 792.

[94] *Ibid.*, 1074.

[95] *Ibid.*, 977.

[96] *Ibid.*, 252.

[97] *Ibid.*, 252.

[98] *Ibid.*, 356.

[99] *Ibid.*, 1908, i, 61.

[1] *Ibid.*, 1907, i, 735.

[2] *Ibid.*, 967.

[3] *Ibid.*, 833.

[4] *Ibid.*, 1905, i, 576.

[5] *Ibid.*, 1907, i, 445.

[6] *Trans.*, 1907, **91**, 1891.

[7] *Ibid.*, 1359.

[8] *Abstr.*, 1907, i, 159.

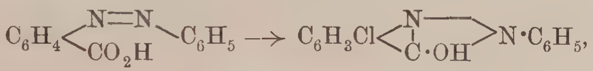
[9] *Ibid.*, 397.

[10] *Ibid.*, 716.

[11] *Ibid.*, 966.

Stoermer and Johannsen,[12] Bülow,[13] and Michaelis,[14] the paper by Stoermer and Martinsen[15] is worthy of attention. Previous work[16] on the conversion of pyrazolones into pyrazoles by phosphorus tribromide has shown that deoxybenzoin is reduced to stilbene and carbostyril to quinoline by the same reagent, and the present work tends to show that the reaction is due to the replacement of hydroxyl by bromine and reaction of the bromine atoms so introduced with hydrogen bromide and excess of phosphorus tribromide.

A synthesis in the related indazole group is given by Freundler,[17] who acts on benzene-2-azobenzoic acid successively with phosphorus trichloride and water.



$$C_6H_4{<}\begin{array}{l}N{=}N\diagdown C_6H_5\\ CO_2H\end{array} \longrightarrow C_6H_3Cl{<}\begin{array}{l}N\text{——}\\ \overset{|}{C}\cdot OH\end{array}{>}N\cdot C_6H_5,$$

but the way in which he explains the mechanism of the reaction is disputed by Tiffeneau.[18]

Windaus[19] has continued his study of the action of ammoniacal zinc hydroxide solution on sugars, and *d*-glucose, *d*-mannose, *d*-fructose, *d*-sorbose, *l*-arabinose, and *l*-xylose have all been found to act in much the same way as glucose, whilst maltose and lactose give smaller yields of a glyoxaline. Rhamnose gives 2 : 4-dimethylglyoxaline in addition to 4-methylglyoxaline, showing that it furnishes acetaldehyde as well as methylglyoxal and formaldehyde on decomposition.

The formulation of histidine as iminazolylalanine is confirmed by Windaus and Vogt,[20] who find that by elimination of the amino-group it is converted into a product identical with a synthesised glyoxaline-4-propionic acid, the latter compound furnishing 4-β-aminoethylglyoxaline when the carboxyl is replaced by the amino-group; Knoop[21] gives a further confirmation of the assigned structure by degradation to glyoxaline.

H. Biltz[22] finds that diphenylglyoxaline is oxidised by potassium permanganate to dibenzoylcarbamide, whilst Sonn[23] has effected a synthesis of benzylmethylglyoxaline, using benzylacetoacetic ester as a starting point.

Amongst keto-derivatives of iminazole, the base prepared by Finger[24] by the interaction of acetiminoethyl ether and glycine ethyl ester,

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[12] *Abstr.*, 1907, i, 966.

[13] *Ibid.*, 986.

[14] *Ibid.*, 246.

[15] *Ibid.*, 446.

[16] *Ibid.*, 1904, i, 181.

[17] *Ibid.*, 1907, i, 158.

[18] *Bull. Soc. chim.*, 1907, [iv], **1**, 1201.

[19] *Abstr.*, 1907, i, 288.

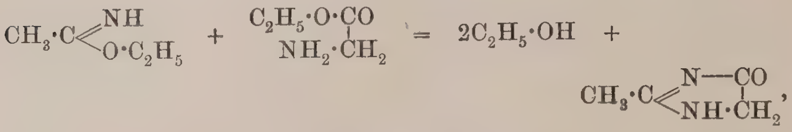
[20] *Ibid.*, 978.

[21] *Ibid.*, 788.

[22] *Ibid.*, 646.

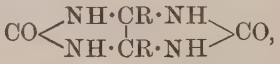
[23] *Ibid.*, 1908, i, 55.

[24] *Ibid.*, 1907, i, 876.



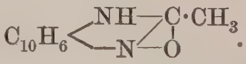
$$CH_3\cdot C{<}\begin{matrix}NH\\ O\cdot C_2H_5\end{matrix} + \begin{matrix}C_2H_5\cdot O\cdot CO\\ NH_2\cdot CH_2\end{matrix} = 2C_2H_5\cdot OH + CH_3\cdot C{<}\begin{matrix}N{-}CO\\ NH\cdot CH_2\end{matrix},$$

is peculiar, inasmuch as it reacts with two molecules of benzaldehyde, the methyl as well as the methylene group taking part in the reaction.

H. Biltz has studied the glyoxalones obtained by the condensation of benzoin with carbamide,[25] and also the acetylenediureine,[26] first obtained by Schiff,[27] from glyoxal and carbamide. This substance, as well as derivatives which have been described by Angeli,[28] seem undoubtedly to possess the constitution,  $CO{<}\begin{matrix}NH\cdot CR\cdot NH\\ NH\cdot CR\cdot NH\end{matrix}{>}CO$, originally assigned to them.

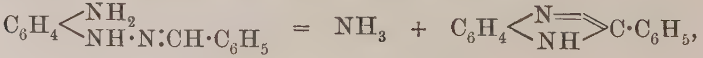
Dieckmann and Kämmerer[29] have obtained derivatives of the nearly allied parabanic acid in examining the action of hydrocyanic acid in phenylthiocarbimide, and of ethyl oxalate on phenylcarbamide.

O. Fischer[30] thinks that the explanation of the second 2-methylnaphthiminazole obtained by Meldola, Eyre, and Lane[31] is given in that the supposed molecule of water of crystallisation is really an oxygen atom which has not been removed during the reduction. This would make the compound possess the constitution:



$$C_{10}H_6{<}\begin{matrix}NH-C\cdot CH_3\\ N-O\end{matrix}.$$

Franzen describes the production of *N*-diaminonaphthiminazole from 2 : 3-naphthalenedihydrazine,[32] and his observation of the formation of 2-phenylbenziminazole by warming benzaldehyde-*o*-aminophenylhydrazone with dilute mineral acids,[33]



$$C_6H_4{<}\begin{matrix}NH_2\\ NH\cdot N{:}CH\cdot C_6H_5\end{matrix} = NH_3 + C_6H_4{<}\begin{matrix}N{=}\\ NH\end{matrix}{>}C\cdot C_6H_5,$$

calls to mind the indole syntheses of Emil Fischer.

Other papers on benziminazole derivatives have appeared from Kym[34] and Brand.[35]

[25] *Abstr.*, 1908, i, 56.

[26] *Ibid.*, 62.

[27] *Ibid.*, 1878, 287.

[28] *Ibid.*, 1890, 1290.

[29] *Ibid.*, 1907, i, 979.

[30] *Ibid.*, 352.

[31] *Trans.*, 1903, **83**, 1185.

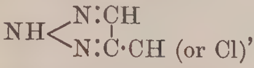
[32] *Abstr.*, 1907, i, 880.

[33] *Ibid.*, 321.

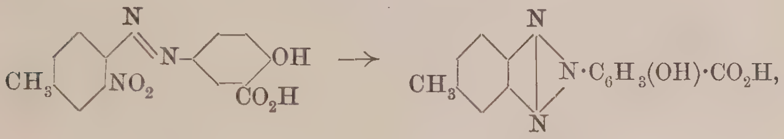
[34] *Ibid.*, 560.

[35] *Ibid.*, 800.

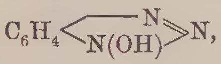
Triazoles.

1 : 2 : 3-Triazoles have been obtained by Peratoner and Azzarello [36] and Tamburello and Milazzo [37] by the action of diazomethane and its homologues on cyanogen and its chloride. The reactions are of the type $CH_2N_2 + C_2N_2$ (or CNCl) =  $\mathrm{NH}{<}\begin{array}{l}\mathrm{N{:}CH}\\ \mathrm{N{:}\overset{|}{C}{\cdot}CH}\ \text{(or Cl)}\end{array}$, and if suitable precautions are not taken the diazo-hydrocarbon reacts further, alkylating the imino-group.

2-Substituted benzotriazoles have been obtained by Grandmougin and Guisan [38] by the reduction of *o*-nitroazo-compounds,



and the azimidols, produced by the action of alkali on *o*-nitro-substituted phenylhydrazines, have been examined by Curtius and his pupils.[39] The first member of this series, benzazimidol,



$$C_6H_4{<}\begin{array}{c}\overline{\qquad N}\\ N(OH)\end{array}{>}N,$$

was described by Nietzki and Braunschweig.[40]

The vexed question of the constitution of the products obtained by the transformation of ethyl diazoacetate seems to be finally settled by the work of Curtius, Darapsky, and Ernst Müller.[41] Bülow first pointed out the great probability of the so-called "dihydrotetrazine" being *N*-aminotriazole, and this is definitely confirmed by the above-named authors, who also show that the bisdiazomethane of Hantzsch and Silberrad is really *C*-aminotriazole, and that the true tetrazine series is represented by the so-called "bisazoxy"-compounds of Hantzsch and Lehmann. The relationships of the different compounds are well shown by a chart given in the second paper quoted above, and the names in brackets are those by which the compounds have been known at various times:

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[36] *Abstr.*, 1907, i, 979.

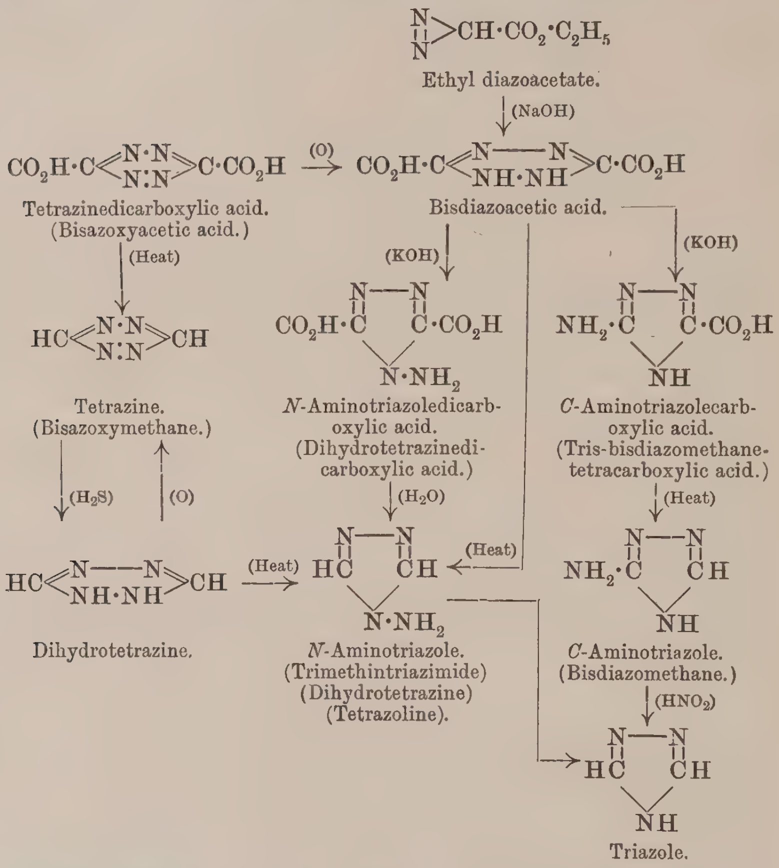
[37] *Ibid.*, 1088.

[38] *Ibid.*, 1092.

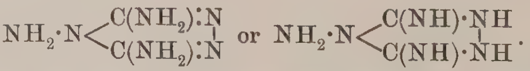
[39] *Ibid.*, 969, 1078.

[40] *Ibid.*, 1895, i, 135.

[41] *Ibid.*, 1907, i, 262, 359, 450, 451.

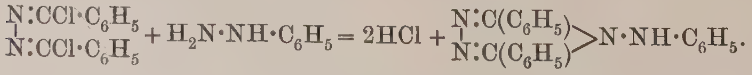

Ethyl diazoacetate.
(NaOH)
Tetrazinedicarboxylic acid. (Bisazoxyacetic acid.)
(O)
Bisdiazoacetic acid.
(Heat)
(KOH)
(KOH)
Tetrazine. (Bisazoxymethane.)
N-Aminotriazoledicarboxylic acid. (Dihydrotetrazinedicarboxylic acid.)
C-Aminotriazolecarboxylic acid. (Tris-bisdiazomethanetetracarboxylic acid.)
(H₂S)
(O)
(H₂O)
(Heat)
(Heat)
(Heat)
Dihydrotetrazine.
N-Aminotriazole. (Trimethintriazimide) (Dihydrotetrazine) (Tetrazoline).
C-Aminotriazole. (Bisdiazomethane.)
(HNO₂)
Triazole.

M. Busch[42] draws attention to the fact that he had recognised the so-called diphenylurazine as *N*-phenylaminotriazole some years back,[43] and Pellizzari and Repetto[44] now think it quite probable that the base, $C_2N_6H_6$, obtained by Pellizzari and Cantoni[45] by the action of cyanogen bromide on aqueous hydrazine is not "guanazine," but 4-aminoguanazole:



$$NH_2\cdot N\left<\begin{matrix}C(NH_2):N\\ C(NH_2):N\end{matrix}\right. \text{ or } NH_2\cdot N\left<\begin{matrix}C(NH)\cdot NH\\ C(NH)\cdot NH\end{matrix}\right. .$$

Stollé has similarly recognised the supposed dihydrotetrazines obtained by the action of primary hydrazines on dibenzoylhydrazide dichloride as *N*-arylaminotriazoles:[46]



$$\begin{matrix}N:CCl\cdot C_6H_5\\ N:CCl\cdot C_6H_5\end{matrix} + H_2N\cdot NH\cdot C_6H_5 = 2HCl + \left.\begin{matrix}N:C(C_6H_5)\\ N:C(C_6H_5)\end{matrix}\right> N\cdot NH\cdot C_6H_5.$$

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[42] *Abstr.*, 1907, i, 564.

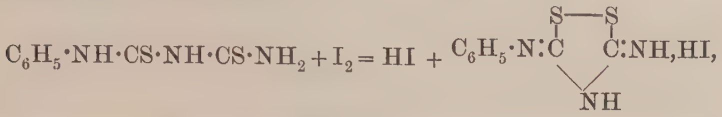
[43] *Ibid.*, 1901, i, 616.

[44] *Ibid.*, 1908, i, 65.

[45] *Ibid.*, 1905, i, 577.

[46] *Ibid.*, 1907, i, 359, 654.

The thiourets obtained by Fromm and Schneider[47] by oxidising the aryldithiobiurets with iodine:



have been used by Fromm and Vetter[48] in the synthesis of triazoles and other ring compounds. Half the sulphur is eliminated by the action of aromatic amines, open-chain compounds possessing the constitutions

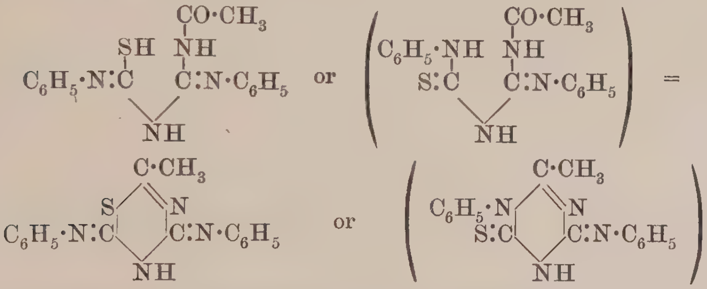
$$C_6H_5{\cdot}N{:}C(SH){\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}C_6H_5$$

and

$$C_6H_5{\cdot}N{:}C(SH){\cdot}NH{\cdot}C({:}NH){\cdot}NH{\cdot}NH{\cdot}C_6H_5,$$

respectively being produced by the action of aniline and phenylhydrazine.

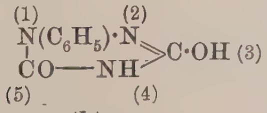
The acetyl derivative of the first condensation product loses water on boiling with alcohol and potash, and the resulting compound is formed according to the equation:



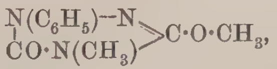
The compound produced from phenylhydrazine loses hydrogen sulphide on heating, giving 3-amino-5-anilino-1-phenyltriazole.

Fromm and von Göncz[49] publish a further triazole synthesis, potassium cyanoiminodithiocarbonate, $(KS)_2C{:}N{\cdot}CN$, being used as initial material; it may be converted into the corresponding dibenzyl ester, which then condenses with phenylhydrazine giving 5(or 3)-amino-3(or 5)-thiobenzyl-1-phenyltriazole.

An interesting study of dynamic isomerism has been made by Acree[50] in the case of phenylurazole and its 4-methyl derivative. Several tautomeric formulæ are possible; the substance behaves, however, as if it had the structure (I):



(I.)



(II.)

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[47] *Abstr.*, 1906, i, 714.

[48] *Ibid.*, 1907, i, 982.

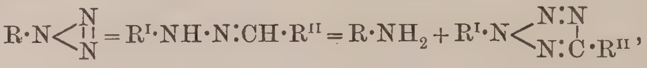
[49] *Ibid.*, 872.

[50] *Ibid.*, 258, 796.

for the dissociation constants of the 2 : 3- and 4 : 5 amido-groups are $K=0{\cdot}00001$ and $K=0{\cdot}0000005$ respectively, a result which is confirmed by the conversion of the substance into a dimethyl ether of structure (II) by the action of diazomethane.

Tetrazoles.

Dimroth and Merzbacher[51] find that tetrazoles are produced by the interaction of arylazoimides and the phenylhydrazones of aldehydes:



$$R{\cdot}N{<}\begin{matrix}N\\ \|\\ N\end{matrix} = R^{I}{\cdot}NH{\cdot}N{:}CH{\cdot}R^{II} = R{\cdot}NH_2 + R^{I}{\cdot}N{<}\begin{matrix}N{:}N\\ \quad |\\ N{:}C{\cdot}R^{II}\end{matrix},$$

and Wieland and Bauer[52] incidentally touch on the tetrazole and tetrazine groups in studying the action of alkalis on dihydroxyguanidine. The reaction gives an "aminoazaurolic acid,"

$$ON{\cdot}C(NH_2){:}N{\cdot}NH{\cdot}C(NH_2){:}N{\cdot}OH,$$

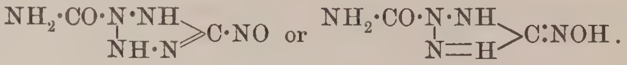
the name calling to mind the "azaurolic acids" [for example,

$$CH_3{\cdot}C(NO){:}N{\cdot}NH{\cdot}C({:}N{\cdot}OH){\cdot}CH_3]$$

obtained by Victor Meyer as reduction products of nitrolic acids. The aminoazaurolic acid yields *iso*nitrosoaminodihydrotetrazine when boiled with 18 per cent. hydrochloric acid, and undergoes partial hydrolysis on reduction, hydrazodicarboxylamideoxime,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C(NH_2){:}NOH,$$

being produced. By the action of nitrous acid, a cyclic compound is formed, constituted probably as:



$$\begin{matrix}NH_2{\cdot}CO{\cdot}N{\cdot}NH\\ \qquad\quad |\\ \qquad\quad NH{\cdot}N\end{matrix}{>}C{\cdot}NO \quad \text{or} \quad \begin{matrix}NH_2{\cdot}CO{\cdot}N{\cdot}NH\\ \qquad\quad |\\ \qquad\quad N{=}H\end{matrix}{>}C{:}NOH.$$

When tetrazole itself is treated with benzoyl chloride in pyridine solution, it undergoes fission, nitrogen is eliminated, and dibenzoylcarbamide produced. Heller[53] further finds that, although no action takes place in the cold, when tetrazole and benzoyl chloride are warmed, dibenzoylhydrazine is formed; the same compound being also obtained from 1 : 2 : 4-triazole.

Furan and Furazan.

Very few syntheses are to be noted in this group, Ludwig[54] has obtained dialkyldihydrobenzofurans by the action of the Grignard reagent on phthalide; Fromherz and Meigen[55] have prepared and examined the *syn-* and *anti-*oximes of methylfurfuraldehyde, whilst

[51] *Abstr.*, 1907, i, 659.

[52] *Ibid.*, 491.

[53] *Ibid.*, 261.

[54] *Ibid.*, 702.

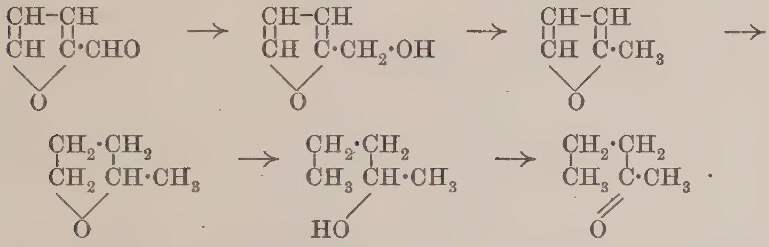
[55] *Ibid.*, 232.

diphenylene oxide (and carbazole) have been condensed with phthalic anhydride by Stümmer.[56]

von Kostanecki and Lampe [57] find that reduction effects a fission of the furan ring in the tetramethyl ether of catechin, a reaction corresponding with Alexander's [58] production of coumaran and *o*-ethylphenol by the reduction of coumarone with sodium and alcohol. The two authors named have further examined the halogen substitution products of the tetramethyl ether [59] and, conjointly with Marschalk,[60] synthesised some compounds which must be nearly related to catechin.

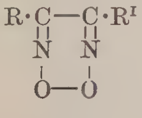
Tannin has formed the subject of further discussion, Nierenstein [61] considering that, as its acetyl derivative only contains five acyl groups, Dekker's formula,[62] which corresponds with the possibility of a hepta-acetyl compound, cannot be correct.

The hydrogenisation of the furan nucleus has been effected by Padoa and Ponti,[63] who passed furfuraldehyde vapour mixed with hydrogen over reduced nickel at 225°. The course of the reduction is illustrated by the following scheme:

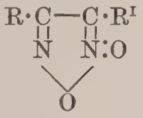


The methylfuran and secondary amyl alcohol were detected, the furyl alcohol and methyltetrahydrofuran isolated and analysed, whilst the methyl propyl ketone was separated as its semicarbazone.

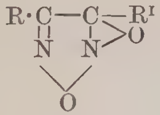
The furazan compounds may be mentioned here;[64] Wieland suggested some time back that the glyoxime peroxides, which have generally been represented as possessing structure (I), are more probably furazan oxides (II):



(I.)



(II.)



(III.)

Quite recently,[65] he has come to the conclusion that formula (III) is

[56] *Abstr.*, 1907, i, 723.
[57] *Ibid.*, 334.
[58] *Ibid.*, 1892, 1318.
[59] *Ibid.*, 1908, i, 86.
[60] *Abstr.*, 1907, i, 950.
[61] *Ibid.*, 331.
[62] *Ann. Report*, 1906, 167.
[63] *Abstr.*, 1907, i, 146.
[64] *Ibid.*, 1904, i, 54.
[65] *Ibid.*, 1908, i, 108.

to be preferred, and shows that the "glyoxime peroxides" are converted into the corresponding furazans by the action of phosphorus pentachloride.

Thiophen and Thiazoles.

By the action of mercuric acetate on thiophen, Dimroth[66] obtained a compound to which he gave the constitution

$$C_4H_2(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)(HgOH)S;$$

this is corrected by Paolini,[67] who uses the substance for the isolation of thiophen, to $C_4H_4(Hg{\cdot}O{\cdot}CO{\cdot}CH_3)_4S$.

Fromm and Schmoldt[68] describe several syntheses of "thionessal" (tetraphenylthiophen) showing that it may be produced by the dry distillation of sodium thiobenzoate, and Fromm and Höller[69] examine the results obtained by Engler[70] from distillation of the product of the action of hydrogen sulphide on acetophenone. Fromm and Höller find that it is neither a thiopinacone nor disulphide, but a mixture of sulphur and 2 : 4-diphenylthiophen.

von Walther and Greifenhagen[71] have obtained substituted thiazolines by the interaction of bromoacetophenone and diarylthiocarbamides, thiocarbamides, or thiourethanes.

iso*Oxazolones.*

In addition to the work of Moureu and Lazennec already referred to under pyrazolones, we may note the production of oximinophenyl-*iso*oxazolone by Wahl from ethyl *iso*nitrosobenzoylacetate,[72] and Reissert's production of anthranil by the decomposition of *o*-nitrodimercuribenzylidene oxide, $NO_2{\cdot}C_6H_4{\cdot}CH{:}Hg_2{:}O$, with hydrochloric acid.[73]

Pyridine and Piperidine.

The behaviour of piperidine vapour and of pyridine vapour mixed with hydrogen towards reduced nickel has been examined by Sabatier and Mailhe[74] as well as by Padoa.[75] The authors find that piperidine gives pyridine, but pyridine and hydrogen do not give piperidine; in the deviation from the behaviour of benzene, Sabatier and Mailhe see an argument against Körner's pyridine formula.

The wandering of alkyl groups in the pyridine series has engaged the attention of H. Meyer[76]; the first observation that 4-methoxypyridine gave *N*-methylpyridone at 220° being due to Haitinger and Lieben.

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[66] *Abstr.*, 1899, i, 428.

[67] *Ibid.*, 1907, i, 788.

[68] *Ibid.*, 702.

[69] *Ibid.*, 710.

[70] *Ber.*, 1895, **28**, 895.

[71] *Abstr.*, 1907, i, 349, 551.

[72] *Ibid.*, 217.

[73] *Ibid.*, 1103.

[74] *Ibid.*, 549.

[75] *Ibid.*, 636.

[76] *Ibid.*, 343.

Somewhat similar changes with the esters of pyridinecarboxylic acids were observed by Kirpal;[77] for instance, apophyllenic acid is produced by the isomerisation of either of the acid monoethyl esters of cinchomeronic acid. Meyer has now examined several acids derived from pyridine and quinoline containing alkyloxy-groups in the 2- and carboxyl in the 3-, 4-, or 5-position, but in no case was a wandering of the alkyl to nitrogen observed, although where the carboxyl and methoxyl groups are in the meta-position relatively to one another the methyl group wanders so as to give a carboxylic ester.

Zincke publishes with Schreyer[78] a further communication on the transformation products of dinitrophenylpyridinium chloride; Barthe[79] describes new mono- and tri-bromopyridines, whilst B. Oddo,[80] in examining the compounds of pyridine and quinoline with magnesium phenyl bromide, finds that one molecular proportion of the latter unites with one, two, or three molecules of quinoline. New stilbazoles are described by Ahrens and Luther[81] and Löwensohn,[82] whilst Ortoleva[83] continues his study of the substance obtained by the action of iodine on a pyridine solution of benzaldehydephenylhydrazone.

The physical properties of pyridine derivatives have engaged some attention. F. Baker and Baly[84] find that introduction of methyl groups or chlorine atoms into the pyridine nucleus, whilst it reduces the oscillation frequency, does not alter the type of the absorption. From the absorption spectra of the hydroxypyridines, it is concluded that the β-compound is phenolic, but that the α- and γ-derivatives are pyridones.

Kirpal[85] has determined the dissociation contents of the isomeric ester-acids produced by quinolinic and cinchomeronic acids, and Kailan[86] has measured the velocity of esterification of pyridinemonocarboxylic acids by alcoholic hydrogen chloride.

A number of tetrahydropyridine bases are described by W. Koenigs, Bernhart, and Ibele,[87] whilst K. Löffler[88] has (in conjunction with Plöcker, Grosse, and Grunert) prepared a number of conidine bases, the attempt at synthesising conidine itself being unsuccessful.

A piperidine synthesis from ethyl acetonedicarboxylate, aldehydes, and primary amines is given by Petrenko-Kritschenko and M. Lewin,[89] and Gabriel and Colman[90] find that, when the isomerisation product of 1-γ-chloropropylpiperidine is distilled with potash, some 1-γ-hydroxy-

[77] *Abstr.*, 1902, i, 564; 1903, i, 117, 852.
[78] *Ibid.*, 1907, i, 625.
[79] *Ibid.*, 792.
[80] *Ibid.*, 549, 668.
[81] *Ibid.*, 965.
[82] *Ibid.*, 1908, i, 51.
[83] *Ibid.*, 729.
[84] *Trans.*, 1907, **91**, 1122.
[85] *Abstr.*, 1907, i, 722.
[86] *Ibid.*, ii, 678.
[87] *Ibid.*, 1907, i, 791.
[88] *Ibid.*, 437, 439, 440, 441.
[89] *Ibid.*, 708.
[90] *Ibid.*, 237.

propylpiperidine is produced. In this, they see a further proof that the condensation product of 1-γ-propylpiperidine is unimolecular. Other work which bears on this question is contained in a paper by J. von Braun[91] on the action of piperazine on $\alpha\epsilon$-dihalogenpentanes.

Finally, Franchimont, van Rijn, and Friedmann[92] have studied the action of nitric acid on various piperidides, and find that those of succinic and sulphuric acids give nitropiperidine.

Quinoline.

Blaise and Maire[93] find that 4-alkylquinolines can be readily prepared by heating aniline with ketones containing a β-chloroethyl radicle; von Niementowski[94] finds 4-anilino-2-hydroxyquinoline amongst the products of interaction of ethyl benzoylacetate and anthranilic acid, whilst O. Stark,[95] in an attempt to dehydrate the oxime of 3-acetyl-2-methylquinoline, obtained 3-amino-2-methylquinoline as the result of a Beckmann transformation accompanied by hydrolysis of the acetyl groups.

B. Oddo[96] finds that, not only does magnesium phenyl bromide combine with different molecular proportions of quinoline, but that, when bromobenzene, quinoline, and magnesium are allowed to interact in toluene solution, 2-phenylquinoline is produced.

L. J. Simon and Mauguin,[97] examine the mechanism of Döbner's reaction, and employ α-naphthylamine, pyruvic acid, and benzaldehyde as components; H. Meyer and Turnau[98] give details of the preparation of quinoline-2-carboxylic chloride by means of thionyl chloride, whilst Ornstein[99] extends the work of Mulert[1] and Pfitzinger[2] on derivatives of 3-methylcinchonic acid. In a paper on cases of steric hindrance among alkyl substituted cinchonic acids, Hans Meyer[3] incidentally corrects a number of errors in the dissertations of Ornstein (Berlin, 1904) and Mulert (Berlin, 1904).

Acridine.

Senier, with Austin,[4] has investigated the conditions under which mixed phenonaphthacridines may be obtained by the methylene iodide method and, with Compton,[5] the production of simpler substituted acridines when methylene chloride is used. Bucherer and Seyde[6] employ formaldehyde and nitrous acid with diarylamines, and A. E. Dunstan and Hilditch have condensed diphenylamine with *p*-bromo- and chloro-benzoic acids.

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[91] *Abstr.*, 1907, i, 728.

[92] *Ibid.*, 842.

[93] *Ibid.*, 241.

[94] *Ibid.*, 1081.

[95] *Ibid.*, 973.

[96] *Ibid.*, 549.

[97] *Ibid.*, 725.

[98] *Ibid.*, 344.

[99] *Ibid.*, 443.

[1] *Ibid.*, 1906, i, 534.

[2] *Ibid.*, 1903, i, 53.

[3] *Ibid.*, 1907, i, 342.

[4] *Trans.*, 1907, **91**, 1233, 1240.

[5] *Ibid.*, 1927.

[6] *Abstr.*, 1907, i, 344.

In the production of acridones, aryl substituted anthranilic acids are necessary, and the conditions under which the chlorine in *o*-chlorobenzoic acid may be replaced by arylamino-groups have been studied by Ullmann.[7] The best catalyst is a small quantity of a copper salt, and Irma Goldberg and Marie Nimerovsky[8] find that the presence of a small quantity of copper enables the further phenylation of anthranilic acid to diphenylanthranilic acid. It is necessary, however, to use iodobenzene as bromobenzene is inactive.

A number of acridones have been prepared from the arylaminobenzoic acids mentioned, and Ullmann (*loc. cit.*) finds that, whilst the introduction of halogens into the acridone molecule has practically no effect on the fluorescence, this property is nearly inhibited by nitro-groups. Of the aminoacridones, the 2- and 4-derivatives fluoresce strongly in alcoholic solution, whilst the 1-amino-compound does not; on addition of hydrochloric acid, the conditions are reversed, the fluorescence of the 2- and 4-compounds disappearing, whilst the 1-aminoacridone hydrochloride exhibits the property.

Goldberg and Nimerovsky (*loc. cit.*) have obtained the hitherto unknown 10-phenylacridone from the dehydration of diphenylanthranilic acid, and Ullmann and Maag[9] find that the substance gives a colourless carbinol base with magnesium phenyl bromide which dissolves in acids, giving solutions of acridinium salts; these possess a yellow colour and green fluorescence. In a later paper,[10] Ullmann, Bader, and Labhardt find that acridine itself readily condenses with dimethylaniline in presence of phosphoryl chloride to furnish 5-*p*-dimethylaminoacridine.

Diazines.

Paal and Kühn[11] continue the synthesis of *o*-diazines, whilst the *m*-diazines, since they include the pyrimidines, have engaged much attention. The most important syntheses in the latter group are due to T. B. Johnson, H. L. Wheeler, and their co-workers (F. W. Heyl, C. O. Johns, and C. F. Speh),[12] and an example of the method employed by these chemists was given in last year's Report (p. 173). Studies are being made of the behaviour of various carboxylic acids of the series towards hot 20 per cent. sulphuric acid with the view of obtaining information as to the manner in which the pyrimidines are bound up to the nuclein molecules.

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[7] *Abstr.*, 1907, i, 842.

[8] *Ibid.*, 621.

[9] *Ibid.*, 638.

[10] *Ibid.*, 1908, i, 52.

[11] *Ibid.*, 1908, i, 57.

[12] *Ibid.*, 1907, i, 559, 728, 877, 879, 972, 1083; 1908, i, 59.

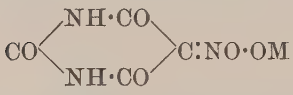
As an example, cytosine-5-carboxylic acid is found to be converted into uracil-5-carboxylic acid by the treatment whereby cytosine is isolated from the nucleic acids. Evidently, then, the latter substances cannot contain the cytosine-5-carboxyl grouping.

In order to find out whether some of the pyrimidine derivatives obtained by the hydrolysis of nucleic acids with moderately concentrated sulphuric acid may not be formed from purine bases by hydrolysis and reduction, Burian[13] has heated dextrose with diluted sulphuric acid (30—40 per cent.), adenine, and guanine. The result is positive, 6-aminopyrimidine being obtained from the first base, and 2-amino-6-oxypyrimidine (*iso*cytosine of Wheeler and Johnson) from the second.

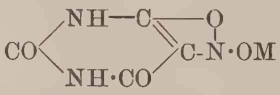
The oxidation of uracil derivatives has been studied by Hoebel[14] and Offe,[15] the work being a continuation of that of Behrend.[16]

The colours exhibited by the condensation products of aromatic aldehydes with diphenylbarbituric acid obtained by Miss Whiteley[17] are striking, the benzylidene derivative of 1 : 3-diphenylbarbituric acid occurring in two forms, one yellow and the other colourless ; the diphenylmethylene derivative is yellow, whilst the product from cinnamaldehyde is orange-yellow.

Hantzsch[18] assigns the respective formulæ :



and



to the colourless and coloured salts of nitrobarbituric acid.

Tafel and H. B. Thompson[19] have submitted 5 : 5-diethylbarbituric acid (veronal) to electrolytic reduction ; it is more difficult to reduce than barbituric acid itself, and, instead of giving a hydrouracil, furnishes 4 : 6-diketo-5 : 5-diethylhexahydropyrimidine. Einhorn and von Diesbach[20] find that veronal is not attacked by sodium amalgam, but the corresponding diethylthiobarbituric acid is readily reduced by this reagent, a portion of the substance undergoing fission, and another portion giving the hexahydropyrimidine compound described by Tafel and Thompson, whilst the remainder forms a condensation product which is probably bisdiethylmalonyltetraminoethane. A · 2-phenyl derivative of Tafel and Thompson's product has been produced by Burrows and Keane,[21] who condensed diethylmalonamide and benzaldehyde in presence of hydrochloric acid.

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[13] *Abstr.*, 1907, i, 735.

[14] *Ibid.*, 557.

[15] *Ibid.*, 645.

[16] *Ibid.*, 1900, i, 120 ; 1903, i, 739 ; 1906, i, 310.

[17] *Trans.*, 1907, **91**, 1330.

[18] *Abstr.*, 1907, i, 500.

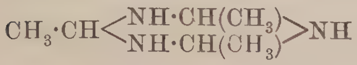
[19] *Ibid.*, 1908, i, 58.

[20] *Ibid.*, 110.

[21] *Trans.*, 1907, **91**, 269.

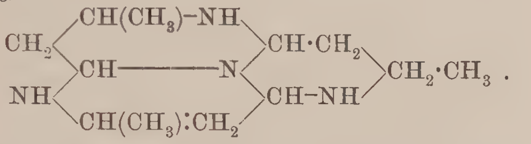
Franchimont and Friedmann[22] find that hydrouracil and trimethyleneureine yield mono- and di-nitramines respectively, a support of Franchimont's theory that the replacement of the hydrogen of an imino-group by the nitro-group is conditioned by the imino-group being situated between a carboxyl and the residue of a saturated hydrocarbon.

Delépine[23] regards aldehyde-ammonia as the hydrate of a cyclic compound, triethylidenetriamine, and the hexaethylidenetetramine as also possessing cyclic structure. The respective formulæ are :



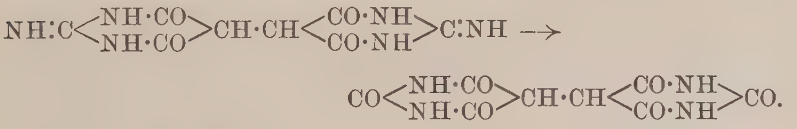
$$CH_3\cdot CH\left<\begin{matrix}NH\cdot CH(CH_3)\\ NH\cdot CH(CH_3)\end{matrix}\right>NH$$

and



In the purine group, Tafel's work on the electrolytic reduction of uric acid (*iso*purone, jointly with Houseman[24]), theophylline, and paraxanthine (with Dodt[25]) may be noted, whilst H. Schulze has studied the action of magnesium phenyl bromide on caffeine and certain derivatives.[26]

Hydurilic acid, which was discovered amongst the products of interaction of nitric and uric acids by Schiefer,[27] has finally been synthesised by Conrad.[28] The guanide obtained by condensation of ethyl ethanetetracarboxylate is the di-imide of hydurilic acid, which it furnishes on heating to 156° with dilute hydrochloric acid :



$$NH{:}C\left<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}\right>CH\cdot CH\left<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}\right>C{:}NH \longrightarrow$$

$$CO\left<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}\right>CH\cdot CH\left<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}\right>CO.$$

Amongst quinazolines, a number have been synthesised by Bogert[29] and his co-workers, Wiggin, Sinclair, Seil, and Nelson.

Paradiazines.

Pyrazine, $C_4H_4N_2$, has been obtained from quinoxaline by Gabriel and Sonn,[30] the latter compound being oxidised by alkaline permanganate to pyrazinedicarboxylic acid, from which carbon dioxide is subsequently removed.

[22] *Abstr.*, 1907, i, 877.

[23] *Ibid.*, 484.

[24] *Ibid.*, 984.

[25] *Ibid.*, 984.

[26] *Ibid.*, 545.

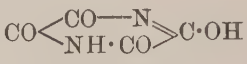
[27] *Annalen*, 1845, **55**, 251 ; 1845, **56**, 1.

[28] *Abstr.*, 1907, i, 985.

[29] *Ibid.*, 351, 560, 660.

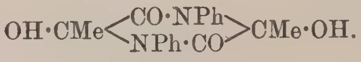
[30] *Ibid.*, 1908, i, 60.

Both oxalimide and the anilide of pyruvic acid have been referred to the piperazine series, de Mouilpied and Rule [31] ascribing to the former the constitution (I), whilst Wohl and Lips [32] give the latter, structure (II):



$$CO<\begin{matrix}CO—N\\NH\cdot CO\end{matrix}>C\cdot OH$$

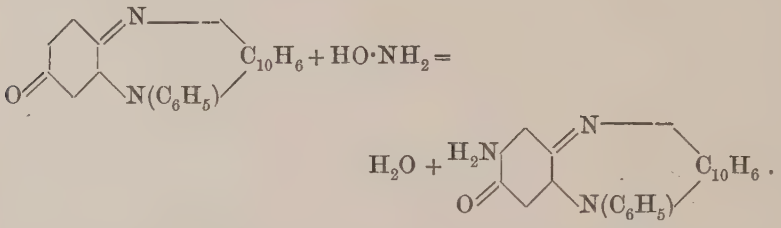
(I.)



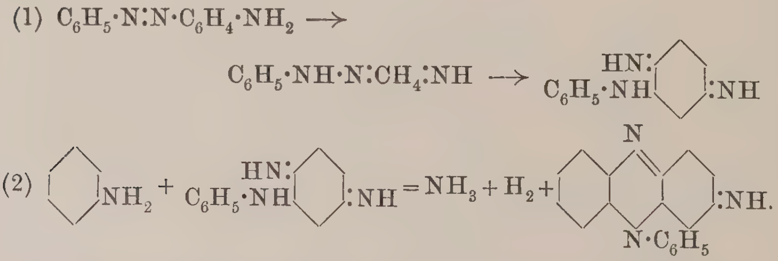
$$OH\cdot CMe<\begin{matrix}CO\cdot NPh\\NPh\cdot CO\end{matrix}>CMe\cdot OH.$$

(II.)

Amongst the azine colouring matters, O. Fischer and Römer [33] confirm Kehrmann and Prager's view [34] that, when hydroxylamine reacts with *iso*rosindone, the amino-group enters the ortho-position to the quinonoid oxygen of the benzene nucleus and not the naphthalene half of the molecule as at first supposed: [35]



Barbier and Sisley [36] prepare aposafranine by heating *p*-aminoazobenzene hydrochloride with aniline, its hydrochloride, and water at 160—170°; they give the following explanation of the mechanism of the reaction:



R. Scholl has published several further papers on indanthrene,[37] and has elucidated the structure of the flavanthrene discovered by R. Bohn amongst the products of fusion of β-aminoanthraquinone with potash. The probability of the substance possessing the constitution required by the equation:

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[31] *Trans.*, 1907, **91**, 176.

[32] *Abstr.*, 1907, i, 583.

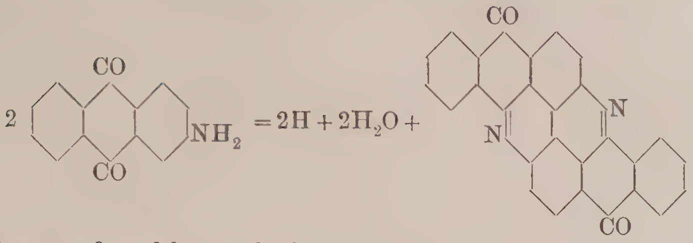
[33] *Ibid.*, 981.

[34] *Ibid.*, 447.

[35] *Ibid.*, 94.

[36] *Ibid.*, 563.

[37] *Ibid.*, 255, 256, 354.



has been confirmed by synthesis.

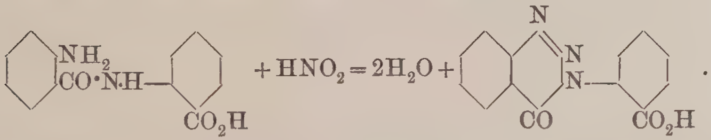
Triazines.

Derivatives of 1 : 2 : 3-triazines (triazones) have been produced by H. Meyer[38] by the action of nitrous acid on the aromatic analogues of polypeptides. The latter substances are prepared by the action of *o*-nitrobenzoyl chloride on lithium anthranilate:

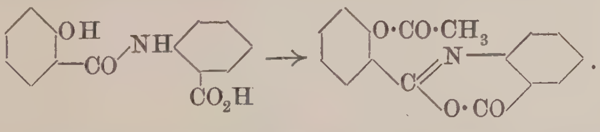
$$NO_2{\cdot}C_6H_4{\cdot}COCl + NH_2{\cdot}C_6H_4{\cdot}CO_2Li = LiCl + NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$$

(repetition of the process if desired) and, finally, reduction of the nitro- to an amino-group.

The action of nitrous acid may be expressed by the equation:



This compound is ruptured by hydrogen chloride to a diazonium salt and, finally, salicylanthranilic acid, which condenses with acetic anhydride in the following manner:



1 : 2 : 3-Triazine derivatives have been prepared by Bailey and Knox[39] and M. Busch and Meussdörffer[40]; Ley and F. Müller[41] have synthesised a dihydro-1 : 3 : 5-triazine derivative, and Finger[42] has prepared the trihydrazide of cyanuric acid and some of its derivatives.

Pyrone Group.

Blaise and Gault[43] publish several papers on pyran and pyrone derivatives from αε-diketopimelic acids. The attempt of Fleischmann[44] to obtain a γγ-dipyrone by condensation of triacetic lactone with acetoacetic ester or β-aminocrotonic ester proved unsuccessful, a lactone being produced instead, whilst Collie and Hilditch[45] find that when dehydracetic acid is heated with sulphuric acid of 85 instead of 90 per cent. very little triacetic lactone is formed, but a substance, $C_8H_8O_4$, which decomposes nearly quantitatively at 200° into dimethylpyrone and carbon dioxide is chiefly obtained. The formula

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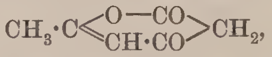
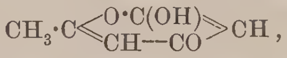
[38] *Abstr.*, 1907, i, 317.
[39] *Ibid.*, 801.
[40] *Ibid.*, 448.
[41] *Ibid.*, 730.
[42] *Ibid.*, 298.
[43] *Ibid.*, 148, 181, 332.
[44] *Trans.*, 1907, **91**, 250.



$$\mathrm{CH_3\cdot C}<\begin{matrix}\mathrm{O-CO}\\ \mathrm{CH\cdot CO}\end{matrix}>\mathrm{CH_2},$$

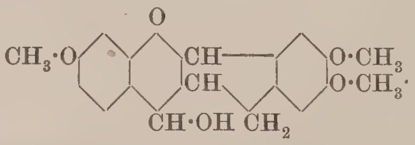
proposed by Collie for the product of the action of sulphuric acid on dehydracetic acid, which in its enolic form would be



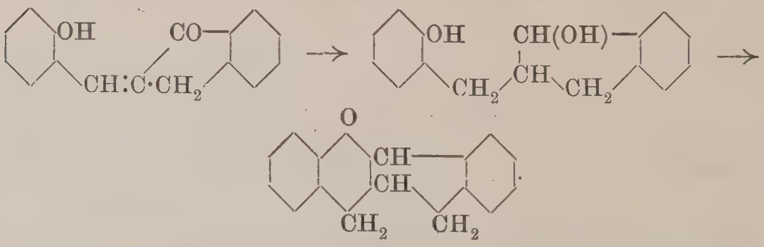
$$\mathrm{CH_3\cdot C}<\begin{matrix}\mathrm{O\cdot C(OH)}\\ \mathrm{CH-CO}\end{matrix}>\mathrm{CH},$$

receives confirmation from Tamburello and Carapelli,[46] who have converted the substance by means of diazomethane into the corresponding methoxymethylpyrone. Bain[47] has examined the behaviour of the disodium derivative of diacetylacetone towards ethylene and propylene dibromides, thus extending his earlier work.[48]

Amongst chroman compounds, W. H. Perkin and R. Robinson[49] have made experiments on the synthesis of compounds nearly related to trimethylbrazilin, which is possibly



Salicylaldehyde and 1-hydrindone condense to give 2′-hydroxy-2-benzylidene-1-hydrindone, which is reduced then to 1 : 2′-dihydroxy-2-benzylhydrindene. Loss of water furnishes 1 : 2-hydrindochroman, the series of changes being represented by the scheme :



By replacing the salicylaldehyde with its *p*-methoxy-derivative and using 5 : 6-dimethoxy-1-hydrindone in place of hydrindone itself, a substance was obtained which, if the above formula for trimethylbrazilin is correct, merely differs from it by a hydrogen atom in place of a hydroxyl group.

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[45] *Trans.*, 1907, **91**, 787.

[46] *Gazzetta*, 1907, **37**, i, 561.

[47] *Trans.*, 1907, **91**, 544.

[48] *Ibid.*, 1906, **89**, 1224.

[49] *Ibid.*, 1907, **91**, 1073.

von Kostanecki[50] publishes further syntheses in the flavone group, starting with cuminaldehyde, and C. Liebermann, S. Lindenbaum,[51] and Truchsäss[52] continue the work on xanthophanic and glaucophanic acids.

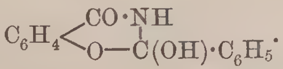
Further syntheses of xanthone derivatives, starting with *o*-chlorobenzoic acids, are published by Ullmann and C. Wagner,[53] and Wichelhaus[54] has examined the action of sulphur on fluorescein.

The question of the constitution of phthalein salts has led R. Meyer and K. Marx[55] to make a spectroscopic comparison of fluorescein and the phthaleins of phenol and quinol in alkaline solution. It is found that the two latter substances are very similar, but differ markedly from fluorescein. Further, Meyer and J. Stark[56] have compared the fluorescent spectra in alcoholic and sulphuric acid solution both in the case of fluorescein and fluoran. With the first compound, the solvent makes little difference, with the second compound the influence of the solvent is most marked, and the result is attributed to formation of oxonium salts, a conclusion arrived at by Hewitt some years back.[57]

That apparently minor differences in constitution can have considerable influence on fluorescent phenomena appears from the description of a number of fluoresceins by Friedl, Weizmann, and Wyler.[58]

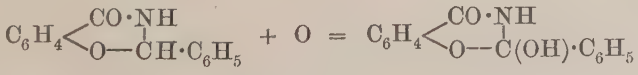
Oxazines.

The labile changes occurring between *O*- and *N*-acylsalicylamides have been ascribed by McConnan and Titherley[59] to cyclic tautomerism, *N*-benzoylsalicylamide being represented in its labile form by the structure:



$$C_6H_4<\begin{matrix}CO\cdot NH\\ O-\overset{|}{C}(OH)\cdot C_6H_5\end{matrix}.$$

This view is controverted by Auwers,[60] but Titherley[61] now shows that the phenylbenzometoxazone obtained by Keane and Nicholls[62] from salicylamide and benzaldehyde can be oxidised in sulphuric acid solution to *N*-benzoylsalicylamide, a result which might be simply expressed by the equation:



$$C_6H_4<\begin{matrix}CO\cdot NH\\ O-\overset{|}{C}H\cdot C_6H_5\end{matrix} + O = C_6H_4<\begin{matrix}CO\cdot NH\\ O-\overset{|}{C}(OH)\cdot C_6H_5\end{matrix}$$

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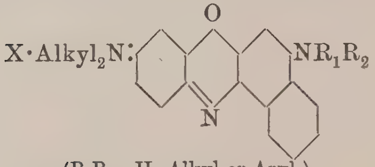
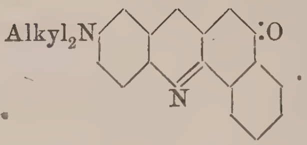
[50] *Abstr.*, 1907, i, 952.
[51] *Ibid.*, 889.
[52] *Ibid.*, 890.
[53] *Ibid.*, 846.
[54] *Ibid.*, 232.
[55] *Ibid.*, 932.
[56] *Ibid.*, ii, 418.
[57] *Ibid.*, 1900, ii, 318.
[58] *Trans.*, 1907, **91**, 1584.
[59] *Ibid.*, 1906, **89**, 1318.
[60] *Abstr.*, 1907, i, 928.
[61] *Trans.*, 1907, **91**, 1419.
[62] *Ibid.*, 264.

Other *p*-oxazines and azoxonium salts are described by Kehrmann and Albert Winkelmann[63] and Nietzki and V. Becker.[64] J. F. Thorpe[65] finds that dye-stuffs of the general formula (I) lose NHR_1R_2 on prolonged boiling with dilute acids, furnishing dialkylaminophenonaphthoxazones (II):



(R_1R_2=H, Alkyl or Aryl.)
(I.)



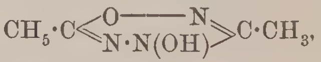
(II.)

Meldola's blue gives the same product, but the reaction in this case necessitates simultaneous oxidation.

Amongst the allied thiazine compounds, Gnehm[66] has studied the action of nitric acid on methylene-blue and its homologues, the tetraethylthionine being far more reactive than the tetramethyl compound (methylene-blue).

Various Rings.

Amongst unclassified cyclic structures, we may note the constitution assigned by Wieland[67] to "hydroxyleucazone,"



$$CH_5{\cdot}C{<}^{O\text{———}N}_{N\cdot N(OH)}{>}C{\cdot}CH_3,$$

the thianthrene compounds of J. Fröhlich,[68] which are derived from *o*-diphenylenedisulphide, $C_6H_4{<}^{S}_{S}{>}C_6H_4$, and the continuation of the work on oxadiazines by Diels and Sasse.[69]

Alkaloids.

A control of the constitutions of tropine, ecgonine, cocaine, and benzoylecgonine has been effected by Gaudechon,[70] who finds that the heats of formation of the alkaloids correspond with the constitutions assigned to them.

Léger[71] has confirmed the constitution of hordenine as *p*-hydroxyphenylethyldimethylamine, for the methiodide of its methyl ether gives *p*-vinylanisole when heated with alkalis, and Willstätter and Heubner[72] find that tetramethyl-$\alpha\delta$-diaminobutane accompanies hyoscyamine in *Hyoscyamus muticus.*

[63] *Abstr.*, 1907, i, 345, 554.

[64] *Trans.*, 1907, **91**, 324.

[65] *Ibid.*, 978.

[66] *Abstr.*, 1908, i, 63, 110.

[67] *Ibid.*, 1907, i, 494.

[68] *Ibid.*, 632.

[69] *Ibid.*, 1086.

[70] *Ibid.*, ii, 738.

[71] *Ibid.*, i, 234, 336.

[72] *Ibid.*, 959.

Barger and Carr[73] have confirmed as a fact the suggestion of Krafft[74] that ergotinine is derived from ergotoxine by removal of the elements of water, and assigns to the two alkaloids the respective formulæ $C_{35}H_{39}O_5N_5$ and $C_{35}H_{41}O_6N_5$.

About two years ago, Pictet made the suggestion that the vegetable alkaloids owe their formation to the following processes :

1. The complex tissue materials, albumin, nucleins, chlorophyll, &c., break down, giving relatively simple products.

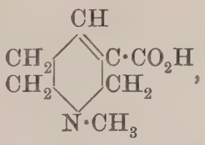
2. These simple bases then condense with other materials to form the more complicated alkaloids.

A systematic examination of various plants with a view of supporting this hypothesis has led to the isolation of pyrrolidine and *N*-methylpyrroline from tobacco, a base, C_5H_9N (probably a *C*-methylpyrroline), from pepper, pyrrolidine and a base, $C_{11}H_{18}N_2$, from carrot leaves, and a base, $C_8H_{15}ON$, from coca, which is, however, not identical with Liebermann's hygrine.

The knowledge of the betel-nut alkaloids has been materially extended by Wohl's researches on amino-acetals and amino-aldehydes.[75] Ammonia reacts with chloropropaldehyde acetal,

$$CH_2{\cdot}Cl{\cdot}CH_2{\cdot}CH(O{\cdot}C_2H_5)_2,$$

giving a mixture of primary, secondary, and tertiary bases. The secondary base by hydrolysis with hydrochloric acid furnishes the hydrochloride of Δ^3-tetrahydropyridine-aldehyde, and if the corresponding *N*-methyl-Δ^3-tetrahydropyridine-aldehyde (obtained by substitution of methylamine for ammonia in the first reaction) is converted into the corresponding carboxylic acid,



it is found to be identical with arecaidine. This alkaloid (and arecoline, its methyl ester) had been previously synthesised by Jahns,[76] but the position of the double linking was unknown.

A. Ladenburg[77] now finds $[\alpha]_D$ 17·85° for pure *iso*coniine ; the value previously obtained (19·2°) was too high, and probable due to admixed allylpiperidine.

Ladenburg states that for a tropeine to possess mydriatic properties, it must contain an acyl group attached to the benzene nucleus, and have an aliphatic hydroxyl in the side-chain. Jowett and Pyman[78] have synthesised a compound of the structure:

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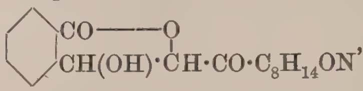
[73] *Trans.*, 1907, **91**, 337.

[74] *Abstr.*, 1906, i, 979.

[75] *Ibid.*, 1908, i, 46.

[76] *Ibid.*, 1892, 737.

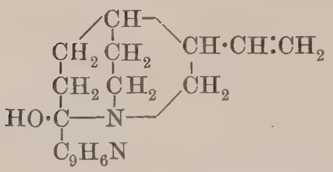
[77] *Ibid.*, 1907, i, 956.



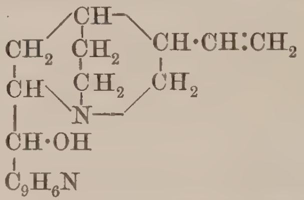
but its physiological action is feeble.

Rabe's formula for cinchotoxine has received ample confirmation, two posthumous papers of W. Koenigs[79] definitely proving the hydrolytic products required by the formula $C_9H_6N\cdot CO\cdot CH_2\cdot CH_2\cdot C_7H_{12}N$ are obtained when Beckmann's transformation is applied to the oxime of Rabe's 1-methylcinchotoxine.[80]

Though the cinchotoxine formula is settled, it should be noted that two possible formulæ remain for cinchonine itself, namely:

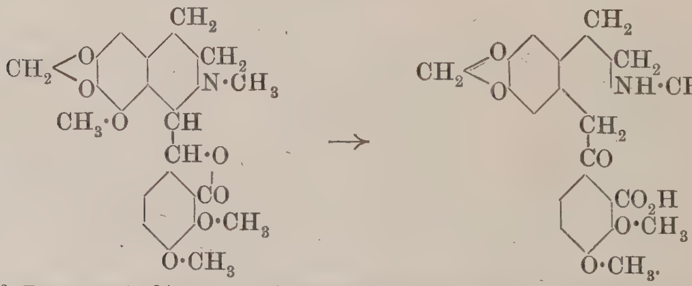


and



P. Rabe[81] finds that when *iso*nitrosomethylcinchotoxine is submitted to the Beckmann reaction, methylcincholeupone nitrile and cinchoninic acid result, whilst he has further investigated the behaviour of cinchonine towards nitric[82] and chromic[83] acids. The substance obtained in the second case is apparently a ketone derived from an alcohol (the cinchonine) by removal of two hydrogen atoms, so that it would appear that the second formula given above for cinchonine is really correct.

Rabe[84] gives us further evidence in favour of this formula, namely, the conversion of narcotine and gnoscopine (racemic narcotine) into a ketone-base, *nornarceine*, by heating with dilute acetic acid; hydrolysis also occurs with formation of cotarnine and meconine, but the change to nornarceine may be represented as follows:



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[78] *Trans.*, 1907, **91**, 92.
[79] Bernhart and Ibele, *Abstr.*, 1907, i, 345, 717.
[80] *Ibid.*, 71.
[81] *Ibid.*, 546.
[82] *Ibid.*, 546.
[83] *Ibid.*, 954.
[84] *Ibid.*, 790.

The analogy to the conversion of cinchonine into cinchotoxine is apparent when one compares the narcotine lactone formula with the secondary alcohol formula for cinchonine.

Rohde and Antonaz [85] find that the sodium derivative of methylcinchotoxine is readily oxidised (by nitrobenzene in alcoholic solution), giving a quinoline-γ-carboxylic acid; the meroquinenine half of the molecule appears, however, in an unworkable condition.

Pictet and Jenny [86] have examined the amine-oxide,

$$C_{23}H_{26}O_5N_2,4\tfrac{1}{2}H_2O,$$

from brucine and hydrogen peroxide; Pavesi [87] has found a new alkaloid, aporeine, in the latex of *Papaver dubium*, and M. Freund [88] has revised Tambach and Jäger's work on narceine.[89]

M. Freund and F. Mayer [90] adopt Gadamer's [91] modification of Perkin's formula for berberine,[92] which makes the free base an aldehyde, but the berberine salts as of quaternary *iso*quinolinium type. The formula of Gadamer would necessitate two asymmetric carbon atoms in an alkyltetrahydroberberine, and Freund and Mayer actually find that, when propyldihydroberberine is reduced, two racemic propyltetrahydroberberines are formed.

The morphine group of alkaloids has been the subject of extensive investigations during the past year by Lees,[93] Knorr and Hörlein,[94] Pschorr,[95] and Vongerichten.[96]

A certain amount of uncertainty as to *iso*morphine (and *iso*codeine), β-*iso*morphine (and β-*iso*codeine), and neo-*iso*- (or γ-*iso*-) morphine (and *pseudo*-codeine) is cleared up by Lees' classification of the genetic relationships:

$$\begin{tikzcd}
\beta\text{-}\textit{iso}\text{Morphine} \arrow[d] & \text{Chloromorphide} \arrow[l] \arrow[r] \arrow[d] & \text{Neo-}\textit{iso}\text{morphine} \arrow[d] \\
\beta\text{-isoCodeine} & \text{Chlorocodide} \arrow[r] & \text{Neo-}\textit{iso}\text{Codeine.}
\end{tikzcd}$$

$$\begin{tikzcd}
\beta\text{-}\textit{iso}\text{Morphine} \arrow[d] & \text{Bromomorphide} \arrow[l] \arrow[r] \arrow[d] & \textit{iso}\text{Morphine} \arrow[d] \\
\beta\text{-}\textit{iso}\text{Codeine} & \text{Bromocodide} \arrow[l] \arrow[r] & \textit{iso}\text{Codeine.}
\end{tikzcd}$$

The nomenclature in the scheme is that used by Lees; in reading Knorr and Hörlein's papers it must be remembered that *iso*morphine is referred to as α-*iso*morphine, β-*iso*codeine as *allo*-ψ-codeine, neo-*iso*-morphine as γ-*iso*morphine, and neo-*iso*codeine as ψ-codeine.

Whilst codeine and *iso*codeine both give codeinone on oxidation,

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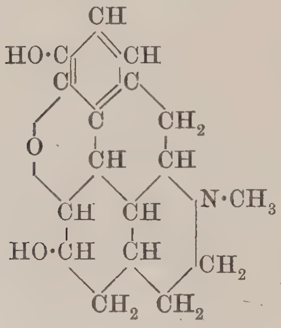
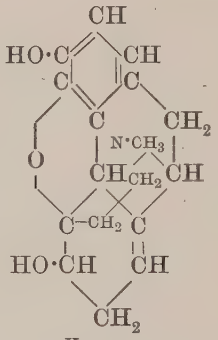
[85] *Abstr.*, 1907, i, 634.
[86] *Ibid.*, 436.
[87] *Ibid.*, 870.
[88] *Ibid.*, 235.
[89] *Ibid.*, 1906, i, 879.
[90] *Ibid.*, 1907, i, 632.
[91] *Ibid.*, 1902, i, 555.
[92] *Trans.*, 1889, **55**, 63; 1890, **57**, 991.
[93] *Ibid.*, 1907, **91**, 1408.
[94] *Abstr.*, 1907, i, 235, 547, 548, 789, 956, 957; 1908, i, 41, 42.
[95] *Ibid.*, 1907, i, 547, 635, 636, 958.
[96] *Ibid.*, 718, 1068.

β-iso- and neo-*iso*-codeines give ψ-codeinone, the two isomeric ketones differing in melting point (187° and 174° respectively) and values of α_D ($-205°$ and $-25°$). Whilst the isomerism of codeine to *iso*codeine is sterical, the same being true of the other pair of (β- and neo-) *iso*-codeines, oxidation of the secondary alcoholic grouping to a ketone makes this form of isomerism disappear, and hence only two codeinones are produced from the four codeines. The codeinones are, however, structurally different, codeinone can be degraded to 3 : 4 : 6-trimethoxyphenanthrene and the 3 : 4 : 8-isomeride being obtained from ψ-codeinone. Evidently some deep-seated change occurs during the formation or hydrolysis of chloro- and bromo-morphides.

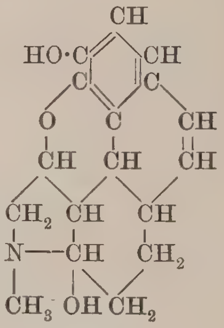
Hitherto both Knorr and Pschorr have been in substantial agreement as to an oxide-bridge between positions 4 and 5 of the phenanthrene nucleus, and the attachment of the nitrogen atom of the chain $CH_3\cdot N\cdot C\cdot C\cdot$ to position 9, but quite recently Bucherer[97] has proposed an entirely novel formula. The three proposed constitutions for morphine are as follows:



Pschorr.

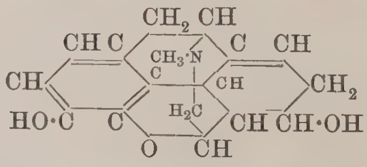


Knorr.



Bucherer.

Bucherer's formula has not yet been thoroughly discussed, but Knorr in a footnote to his last paper[98] thinks that in a modified form (as below) it may be worth considering. Unmodified, it requires



that codeinone and thebainone should be secondary bases, which is at variance with the facts of the case.

J. T. Hewitt.

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[97] *Abstr.*, 1908, i, 43.

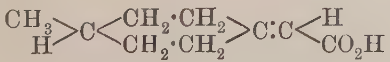
[93] *Ibid.*, 42.

STEREOCHEMISTRY.

The work on stereochemistry published during the past year is voluminous, and is the result of considerable activity on the part of a very large number of investigators; much of the work recorded has served rather to establish more firmly the fundamental theories of this branch of the subject than to break fresh ground for investigation; there are, however, several cases to which this remark does not apply. Notable among the parts of the subject which have received most attention is the quantitative study of optical rotatory power; the results obtained have, however, shown more clearly than ever the enormous influence which the chemical nature of the groups attached to the asymmetric atom may exert on the rotatory power of a compound, an influence which, in some cases, completely outweighs that of the weight of the group. The influence of solvents on rotatory power has also been extensively studied, and there now appears to be some prospect of acquiring a reasonable understanding of these effects, which appear to be due so largely to internal pressure and changes of volume causally related to it.

A very prominent position among the important contributions to this branch of chemistry must be accorded to the work of Fischer, which has thrown some light on that surprising change usually termed the "Walden inversion," and clearly shows the importance of the study of stereochemical changes as a means of elucidating the internal mechanism of chemical reactions, and also to the work of Kipping in adding another element, silicon, to those whose atoms have been shown to be capable of exhibiting optical activity.

The problem attacked simultaneously by Marckwald and Meth and by Perkin and Pope, namely, the production of an optically active compound whose activity, was due to asymmetry of the molecule and not to the asymmetry of any single atom,[1] remains still in the same state as last year. In order to settle the question definitely, both the acids to which the formula



$$\begin{matrix}CH_3\\H\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:C<\begin{matrix}H\\CO_2H\end{matrix}$$

is assigned must be resolved.

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[1] *Ann. Report*, 1906, 185.

The quantitative study of optical rotatory power and its relation to chemical structure has been the subject of a large number of papers, among which the following occur.

Chardin and Sikorski[2] contribute an interesting paper in which they develop Guye's hypothesis and deduce some valuable results.

Guye's original expression for the product of asymmetry involves quantities determining the spatial position of the centre of gravity of each of the four groups attached to the asymmetric carbon atom. In the present state of our knowledge of the forces which determine chemical combination, we have no means of determining these quantities; hence Guye simplified his expression by making two assumptions: (1) that the centres of gravity of the groups are situated on the axes of the asymmetric carbon atom, and (2) that the distance of the centre of gravity of each group from the centre of gravity of the carbon atom is the same, thus obtaining the well-known expression for the product of asymmetry involving only the weights of the four groups.

The enormous mass of statistical evidence accumulated by Guye, Walden, Frankland, and others shows that this expression is inadequate to explain the experimental results. The authors conclude that the first assumption made by Guye is justified, and develop formulæ for the calculation of the "atomic product," that is, the product of the weight of an atom or group and its distance from the carbon atom in certain simple cases. This quantity they find to be a constant for each series in the periodic table.

The further development of the views of these authors will be awaited with interest; but it will be surprising if it can be shown that the "atomic product" is determined by the nature of the group in question alone and is independent of the other groups attached to the carbon atom.

J. J. Thomson[3] discusses the conditions under which a collection of atoms, each consisting of electrified parts rigidly connected together, can exhibit optical activity, and deduces an expression for the optical activity which satisfies the necessary conditions. This theoretical development is, however, inapplicable to concrete cases in the present limited state of our knowledge.

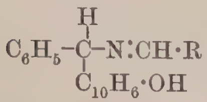
Betti[4] makes an important contribution to our knowledge of the influence of the chemical constitution of a group, as distinct from its weight, on the rotatory power of the asymmetric carbon atom to which it is attached.

This worker has determined the specific rotatory powers in benzene solution of a number of substances having the general formula

[2] *Abstr.*, 1907, ii, 830.

[3] *Proc. Camb. Phil. Soc.*, 1907, **14**, 313.

[4] *Abstr.*, 1907, ii, 661, 726.



$$C_6H_5-\overset{H}{\underset{C_{10}H_6\cdot OH}{C}}-N:CH\cdot R$$

and derived from *d*-α-aminobenzyl-β-naphthol by the action of aromatic aldehydes. The original base was isolated by means of *d*-tartaric acid, and gave $[\alpha]_D + 58\cdot9°$. The compounds formed with twenty-one different aromatic aldehydes were examined; a few only of the more striking results can be mentioned here:

Benzaldehyde compound	$[\alpha]_D + 110\cdot72°$
Salicylaldehyde ,,	,, $-15\cdot65$
p-Hydroxybenzaldehyde compound	,, $+297\cdot3$
o-Methoxybenzaldehyde ,,	,, $+243\cdot6$
p-Methoxybenzaldehyde ,,	,, $+314\cdot4$
o-Nitrobenzaldehyde ,,	,, $-259\cdot36$
p-Nitrobenzaldehyde ,,	,, $+54\cdot29$
5 Bromosalicylaldehyde ,,	,, $-76\cdot37$
5-Bromo-2-methoxybenzaldehyde compound	,, $+39\cdot45$

The remarkable difference between the values of $[\alpha]_D$ for compounds in which the group R has the same weight and differs only in the position of a substituting group in the benzene nucleus is well illustrated in the cases quoted. The hydroxy- or nitro-group in the ortho position to the point of attachment of the radicle R to the asymmetric carbon atom exerts so great an influence on the rotatory power that even its sign is altered; the presence of a methoxy-group in the same position does not have this effect. It may therefore be concluded that the effect is due to a disturbance in the relative positions of the four groups, caused by bringing a group of acidic or electronegative character near the other groups. It is concluded that an electronegative group increases the lævorotation of the molecule, an effect clearly shown in the bromo-derivatives of salicylaldehyde and *o*-methoxybenzaldehyde.

This work clearly shows that Guye's hypothesis in its simplified form could, at best, only apply to small groups of closely allied compounds.

It is interesting to contrast with the work last mentioned, in which the influence of the chemical nature of groups is so prominent, the results obtained by Pickard and Littlebury[5] for the rotatory powers of esters of *l*-menthylcarbamic acid, $C_{10}H_{19}NH\cdot CO_2H$, in which the hydrogen of the carboxyl group is replaced by a group R. This work is a continuation of that described in 1906.[6] The molecular rotatory power of the esters in chloroform solution only varies from 162° to 165·5° when R is a normal aliphatic group, but it may vary from 158° to 169° when R is a secondary aliphatic group, and from 150° to 162°

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[5] *Trans.*, 1907, **91**, 300.

[6] *Ibid.*, 1906, **89**, 94.

when R is an aromatic group either of the benzene or naphthalene series. Similar relations hold for solutions in pyridine and in alcohol and for substituted amides of *l*-menthylcarbamic acid of the type $C_{10}H_{19}NH{\cdot}CO{\cdot}NH{\cdot}R$, where R represents the same alkyl groups; the molecular rotatory power of these compounds is about 160°. Within the range of the small differences observed, the rotation of compounds containing the *o*-tolyl, phenyl, *m*-tolyl, and *p*-tolyl groups increases in the order given, as would be expected from Guye's hypothesis.

The small influence of changes in the constitution of the radicle R is remarkable, and is probably due to the fact that these changes take place relatively far away from the asymmetric carbon atoms in the menthyl complex, so that comparatively little disturbance is produced in the equilibrium positions of the groups attached to the asymmetric carbon atoms in the ring.

Tschugaeff and Sokoloff,[7] by examining the metallic ammines derived from *l*-propylenediamine, add another instance of the great influence of ring formation on rotatory power to those already recorded. Werner came to the conclusion that these compounds had a cyclic structure, and these authors show that the compounds derived from the lævorotatory base are all dextrorotatory.

Patterson and Kaye[8] have now completed the study of the *l*-menthyl diacetyltartrates, which was undertaken with the object of testing the validity of van't Hoff's assumption regarding the summation of the rotatory powers of several asymmetric atoms in a molecule, generally known as the "principle of optical superposition." The theoretical discussion and a criticism of the experimental evidence adduced by Guye and Walden in support of the principle were given in 1906;[9] these authors find that, at 100°,

$[M]_D$ of *l*-menthyl diacetyl-*d*-tartrate = −226°.
$[M]_D$,, ,, -*l*- ,, = −382°.
$[M]_D$,, ,, -*i*- ,, = −280°.

According to the "principle of optical superposition," the rotation of the mesotartrate should be exactly the mean of the *d*- and *l*-tartrates, whereas it differs by 24° or nearly 10 per cent. from this mean.

The difference in solution is still more marked. It must therefore be admitted, in spite of the way in which similar views expressed by M. A. Rosanoff[10] have been criticised by Guye and Gautier,[11] that the principle of optical superposition is not strictly true.

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[7] *Abstr.*, 1907, i, 896.

[8] *Trans.*, 1907, **91**, 705.

[9] *Ibid.*, 1906, **89**, 1884.

[10] *Abstr.*, 1907, ii, 207.

[11] *Ibid.*, 417.

It has usually been concluded from the available experimental evidence that the introduction of an ethylene linking into an optically active compound always increased the rotatory power; the reverse was found to be the case for the change from propyl to allyl[12] in active nitrogen compounds, and also in the allyl and propyl derivatives of tartramide[13] and malamide.[14]

Hilditch[15] has adduced further evidence in support of the above-mentioned conclusion from his experiments on the rotatory powers of the menthyl and bornyl esters of phenylpropionic, cinnamic, and phenylpropiolic acids.

It was found that the change $\gt C{\cdot}C\lt \longrightarrow \gt C{:}C\lt$ produces an increase in the rotatory power, whilst in the removal of another pair of hydrogen atoms, the change $\gt C{:}C\lt \longrightarrow -C{\vdots}C-$ caused a decrease in rotatory power, so that the rotatory power of the compound containing the acetylene linking now became less than that of the saturated compound.

These results agree with those obtained by Walden for the *l*-amyl esters of the same acids as far as the change from saturated to ethylenic linking is concerned, but differ from them as regards the effect of the change from ethylenic to acetylenic linking. The rotatory power of the amyl ester of phenylpropiolic acid is intermediate between that of the cinnamate and the phenylpropionate. This work therefore further emphasises the impossibility of formulating general conclusions concerning a property which is so sensitive to small changes in several factors as optical rotatory power is found to be.

The results of the first of a series of experiments carried out with the object of investigating the possible connexion between the absorption of light and optical rotatory power are described by A. W. Stewart[16]; the particular point to which attention has been directed is the effect of the change from a saturated compound to one containing an ethylene and then an acetylene linking.

There is no connexion between the optical rotatory power and the persistence of the absorption bands when these exist, but in the cases examined there appears to be a relation between the extent of the general absorption and the rotatory power which is stated as a rule "greater rotation greater absorption."

This rule is shown to hold good in certain cases of closely-allied compounds, such as the three acids mentioned above, phenylpropionic, cinnamic, and phenylpropiolic acids and their amyl esters; butyric and crotonic acids and their amyl esters, and other similar cases. That this rule, however, is only applicable within very narrow limits is shown by the fact that itaconic acid has a greater absorptive power than citraconic and mesaconic acids, whereas its amyl ester has a rotatory power between those of the citraconate and mesaconate.

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[12] Thomas and Jones, *Trans.*, 1906, **89**, 310.

[13] Frankland and Twiss, *ibid.*, 1855.

[14] Frankland and Done, *ibid.*, 1859.

[15] *Proc.*, 1907, **23**, 287.

[16] *Trans.*, 1907, **91**, 199.

It is clear also that the absorptive power of an acid cannot always indicate the magnitude of the rotatory power of its esters, since the rotatory powers of the amyl esters of phenylpropionic, cinnamic, and phenylpropiolic acids examined by Walden do not bear the same relation to one another as those of the corresponding menthyl esters examined by Hilditch.

The effect of solvents on the rotatory power of non-electrolytes has occupied the attention of several workers, and a great deal of work on this subject has appeared.

Winther[17] has extended his investigations on the effect of solvents on the rotatory power of active solutes, and now suggests a complete theoretical explanation of these effects.

Ethyl tartrate is found to have a specific rotatory power of +30·4° in solution in formamide at infinite dilution and of −19° in ethylene dibromide under the same conditions; these are respectively the highest positive and negative rotatory powers yet recorded for this substance. The molecular weight of the solute in formamide is normal, whereas in ethylene dibromide the molecules of solute are associated except in very dilute solutions. It is shown that in all solvents except water and formamide, the rotation dispersion-coefficient of nicotine is independent of the solvent and of the concentration; the same is also shown for solutions of ethyl tartrate.

Stress is laid on the part played by internal pressure in altering the rotatory power—the internal pressure of a large number of solvents is calculated by the use of van der Waal's equation and Amagat's data for the compressibility of the liquids.

The author makes three fundamental propositions referring to the effect of solution on active substances: (1) isothermal changes of volume in homogeneous systems are due to change of pressure (internal or external), to change of degree of association, dissociation or state of combination, or to the simultaneous action of two of these;

(2) Every alternation in the rotation of an optically active compound is causally related to a volume change;

(3) Every volume change, which is due to change of pressure *alone*, is accompanied by a change of rotation proportional to the change of volume.

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[17] *Abstr.*, 1907, ii, 831, 832.

Proposition (3) is shown to hold for solutions of nicotine in several solvents, including water, alcohols, ether, and benzene; for camphor in a large number of very different solvents; for *l*-turpentine in several solvents, and for some metallic salts of camphoric acid in water.

When the solvent and solute do not form compounds, then the influence of the former on the rotation of the active solute depends on the difference in their internal pressures. On arranging solvents in the order of the magnitude of their influence on the rotatory power of active solutes, the order is the same for different active solutes. The internal pressure of one liquid can be determined from measurements of the specific gravities of solutions of different concentrations in another liquid whose internal pressure is known. It is concluded that diethyl tartrate has almost the same internal pressure as methyl alcohol.

According to this author, then, *change of volume*, whether caused by temperature, change in degree of association, dissociation, or combination, or by change of pressure, is entirely responsible for the influence of different solvents on the rotatory powers of active solutes. Patterson has, during his long series of researches on the influence of solvents on the rotatory power of ethyl tartrate, repeatedly insisted on the relation of the observed effects to the molecular solution volume of the solute, and has again in a recent paper[18] emphasised the quite secondary part played by association in many cases.

Winther also deals with the rotatory power of electrolytes in aqueous solution; the volume of the active part of the electrolyte is said to remain constant during dissociation, and so the rotatory power is not altered directly by the process of dissociation.

The importance of the study of rotatory power as a method of investigating solutions is pointed out, since this property is the only one which measures the changes of *one* only of the two constituents of a solution.

Many other workers have also contributed to our knowledge of optical rotatory power of solutions; Piutti and Magli[19] describe the determination of the rotatory power of the eight alkyl hydrogen aspartates containing respectively the methyl, ethyl, *n*- and *iso*-propyl, allyl, *n*- and *iso*butyl, and the *iso*amyl-groups. In aqueous solution, these salts are all dextrorotatory at low temperatures and lævorotatory at higher temperatures; the change is due to increasing dissociation as the temperature is raised; the anion is lævorotatory, and the corresponding sodium salts are lævorotatory at all temperatures between 10° and 90° with the exception of the *iso*propyl compound, which only becomes lævorotatory above 22°. The rotatory power is proportional to the concentration of the solution. It is interesting to note that the rotatory power of the allyl compound is less than that of the propyl compound, and also that the rotatory powers of *iso*propyl and *iso*butyl compounds are greater than those of the corresponding normal compounds. The rotatory power, however, does not change regularly with the weight of the alkyl group.

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[18] Patterson and Thomson, *Abstr.*, 1907, ii, 322.

[19] *Abstr.*, 1907, i, 296.

The observations of Pribram[20] and of Shinn[21] indicate that Oudeman's law for electrolytes is not universally true. The last-mentioned observer has examined the rotatory powers of tartrates and of alkaloid salts in very dilute solutions, and concludes that his results cannot be harmonised with the theory of electrolytic dissociation, since the rotatory power frequently does not tend to attain a constant value and the changes observed in these aqueous solutions are very similar to those observed for solutions of substances such as quinine oleate in chloroform. Sherry[22] has determined the rotatory powers of a number of substances, chiefly sugars and alkaloids dissolved in liquid ammonia, liquid sulphur dioxide, or liquid methylamine. These results are interesting, since the solvents are so different from those already examined, yet the rotatory powers of the solutes are often very little different from those observed in ordinary solvents; no mutarotation was observed, and, in ammonia and methylamine, lævulose gave no observable rotation.

Patterson has continued his observations on the influence of solvents on the rotatory power of ethyl tartrate, confining his attention to isomeric solvents or those differing but little in structure.

In a paper by Patterson and McMillan,[23] the rotatory power of ethyl tartrate mixed with the two stereoisomeric (*syn*- and *anti*-) benzaldoximes is shown to differ to a remarkable extent. The rotatory power of a mixture of 90·11 per cent. of ethyl tartrate and 9·89 per cent. of benz*anti*-aldoxime has a rotatory power of 11·38°; this falls gradually to 8·16°, the value for a mixture of the same concentration with the *syn*-oxime. The observation of the change in rotatory power of an active substance can therefore be used to investigate the change of one dynamic isomeride with which it is mixed to another. The same is shown to be the case for mixtures of ethyl tartrate with the anisaldoximes and with ethyl formylphenylacetate.

This surprising difference in the influence of two stereoisomerides on the rotatory power of ethyl tartrate, a difference in the case of the two benzaldoximes greater than that between water and chloroform, led to the investigation by Patterson, Henderson, and Fairlie[24] of the influence of ethyl maleate, fumarate, and succinate on the rotatory power of ethyl tartrate. The specific rotatory power in maleic and fumaric esters is 13·4° and 13·27° respectively at 20° in 20·67 per cent. solution, whilst that in succinic ester is 9·35°. The molecular solution volume of the esters is nearly the same in all three solvents. These results are surprising, since the difference between the maleate and fumarate is so small and yet the difference between the fumarate and succinate is greater than that between the diamyl esters of these acids. It is suggested that these effects may be due to combination of solvent and solute. This method of investigating changes in the constitution of the solvent would therefore be applicable in a limited number of cases only, since in this case two stereoisomerides show practically the same effect.

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[20] *Abstr.*, 1907, ii, 207

[21] *Ibid.*, 417.

[22] *Ibid.*, 920.

[23] *Trans.*, 1907, **91**, 504.

[24] *Ibid.*, 1838.

A few interesting contributions to our knowledge of racemism and racemisation have also appeared during the year. Ladenburg[25] has re-examined the behaviour of the "partially racemic" salt, brucine hydrogen racemate, which crystallises with 2½ molecules of water of crystallisation; the *d*-tartrate is anhydrous, and the *l*-tartrate crystallises with 5 molecules of water of crystallisation. Below 44°, the racemate is less, and above 44° it is more, soluble than the tartrate mixture; hence the salt is only resolved by crystallisation above 44°. Neutral brucine racemate, however, is not resolved at any temperature below 100°.

Up to the present time, no melting-point curve of two substances which form a partially racemic compound has been examined. This lacuna has been filled by Findlay and Miss Hickmans,[26] who have examined the melting points of the *l*-menthyl mandelates; menthyl *r*-mandelate is a partially racemic compound, but undergoes dissociation into its two constituents to the extent of about 50 per cent., which is indicated by the flattened summit of the curve drawn with melting point as ordinate.

A new criterion of racemism has been suggested by Stewart[27] on the basis of his examination of the absorption spectra of active and of externally compensated compounds.

d- and *l*-Tartaric acids show the same absorptive power, which is less than that of racemic acid in concentrated solutions, but the same in dilute solutions. Similarly, dipentene shows greater absorption than *d*- and *l*-limonene.

Difference in absorptive power of the active and externally compensated compounds may therefore be regarded as an indication that the latter is racemic; this method of detecting racemic compounds will be of special value in its application to liquids. Brühl[28] also points out that a difference in the refractive indices and magnetic rotatory powers of the active and externally compensated compounds indicates that the latter is racemic; this is found to be the case for $\Delta^{3:8(9)}$-*p*-menthadiene.

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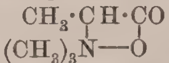
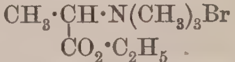
[25] *Abstr.*, 1907, i, 586.

[26] *Trans.*, 1907, **91**, 905.

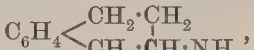
[27] *Ibid.*, 1537.

[28] *Ibid.*, 115.

While collecting material for the study of the "Walden inversion," to which reference is made later in this report, Fischer [29] observed a particularly interesting case of racemisation. Lævorotatory trimethyl-α-propiobetaine,  $\begin{array}{l}CH_3\cdot CH\cdot CO\\ (CH_3)_3N—O\end{array}$, was prepared by the action of trimethylamine on *d*-α-bromopropionic acid and also by the action of methyl iodide on *d*-alanine in alkaline solution.

Now, by the action of trimethylamine on *d*-α-bromopropionic ester, the additive compound,  $\begin{array}{l}CH_3\cdot CH\cdot N(CH_3)_3Br\\ \quad\;\; CO_2\cdot C_2H_5\end{array}$, containing a quinquevalent nitrogen atom, is formed readily at the ordinary temperature. This compound is, however, optically *inactive* and identical with that obtained by the action of trimethylamine on *i*-α-bromopropionic ester. By observing the rotatory power of the mixture during the reaction, it is found that an active additive compound is first formed which can be isolated, and that the racemisation of this is due to the presence of excess of trimethylamine. *d*-Alanine ester, which owes its activity to a similar asymmetric carbon atom which is attached to a tervalent nitrogen atom, is not affected by trimethylamine.

This interesting case of racemisation is somewhat analogous to that observed by Pope and Harvey [30] in tetrahydro-β-naphthylamine,



$$C_6H_4<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH\cdot NH_2\end{array},$$

when this is converted into an acyl derivative or liberated from its salts by alkali, and it is possible that a similar explanation to that suggested in this case may also serve to account for the behaviour of the compound of *d*-α-bromopropionic ester and trimethylamine.

The rather bewildering results obtained in the partial saponification of *l*-menthyl mandelate, in which a dextrorotatory acid was sometimes obtained, whilst in other experiments the acid obtained was lævorotatory, have been further investigated by A. McKenzie and H. A. Müller, [31] and the conditions determining the formation of the one optical isomeride or the other in excess have been clearly established.

l-Menthyl *d*-mandelate is saponified more readily than the *l*-mandelate, so that the *d*-acid should be present in excess in the acid obtained by partial saponification of the ester. Racemisation of the acid also occurs simultaneously, but this is of secondary importance in those cases in which a dextrorotatory acid is obtained.

A dextrorotatory mandelic acid is obtained when *l*-menthyl

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[29] *Abstr.*, 1908, i, 80.

[30] *Trans.*, 1901, **79**, 83.

[31] *Ibid.*, 1907, **91**, 1814.

r-mandelate is partially saponified by dilute caustic potash in the cold, owing to the rate of saponification of the *d*-mandelate being greater than that of the *l*-mandelate and racemisation by the alkali being reduced to a minimum when the alkali is dilute and cold.

A lævorotatory mandelic acid is produced when the same proportions of ester and alkali are heated at 100° in concentrated solution. This is due to the fact that, when saponification has proceeded for some time, there is excess of *l*-mandelate in the unchanged ester, and the potassium mandelate already formed has been racemised by the action of alkali; the racemising action of the alkali, however, is now rapidly diminishing as the concentration of alkali in the solution diminishes, and eventually we have the lævorotatory acid produced in excess from the ester containing excess of *l*-mandelate and this acid retains its activity.

In connexion with the subject of racemisation, it may be mentioned that the allied process which takes place in menthone under the influence of catalysts in which one of the two asymmetric carbon atoms only is affected has now been very fully investigated by Tubandt.[32] This author has now followed the course of the change in a number of different solvents. He concludes that the catalyst forms an additive product with the carbonyl group of the menthone, and that this compound is formed more readily, and consequently inversion occurs more rapidly, the smaller the hydrolytic power of the solvent.

During the year, no method involving a new principle has been added to the methods available for resolving externally compensated compounds into their active constituents, but these methods have been used in the resolution of a number of substances and several very interesting modifications have been introduced.

McKenzie and Thompson[33] and McKenzie and Müller[34] show that pure *d*- or *l*-mandelic acids can be obtained from the mixture of *r*-mandelic acid and one of the optical isomerides, produced by partial saponification of *l*-menthyl or *l*-bornyl mandelate by fractional crystallisation of the acid and its magnesium and cadmium salts from water.

An improved method for the resolution of alcohols has been worked out by Pickard with Kenyon[35] and Littlebury.[36] The acid ester of the alcohol and a dibasic acid, phthalic acid was used, is separated into its two components by fractional crystallisation of a salt formed with an active base, alkaloids or menthylamine were used, and liberation of the active alcohol by saponification. Saponification of these acid esters takes place readily, and this gives the method a further advantage over the menthyl carbamate method (previously described by these authors), since the carbamates are sometimes difficult to hydrolyse. This method has been used for the resolution of *sec.*-octyl alcohol, in which case the menthyl carbamate method had failed to effect resolution. The dextrorotatory alcohol was obtained from the brucine salt of the acid phthalic ester, and the lævorotatory alcohol from the corresponding cinchonidine salt.

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[32] *Abstr.*, 1907, ii, 670.

[33] *Trans.*, 1907, **91**, 789.

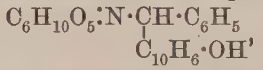
[34] *Loc. cit.*

[35] *Trans.*, 1907, **91**, 2058.

[36] *Ibid.*, 1973.

The method has also been used for the preparation of the four isomeric borneols in a pure state. The constants of the pure compounds are given.

Betti[38] has resolved *r*-α-aminobenzyl-β-naphthol in an interesting way by fractional crystallisation of the compound,



$$C_6H_{10}O_5{:}N{\cdot}\underset{\displaystyle C_{10}H_6{\cdot}OH}{\underset{|}{C}}H{\cdot}C_6H_5,$$

which the base forms with dextrose. The dextrose compound of the *d*-base is the less soluble, and from it the dextrorotatory base can be produced readily by hydrolysis with dilute acid.

Locquin[38] has succeeded in resolving α-amino-β-methylvaleric acid by crystallising the brucine salt of its formyl derivative, a method previously used by Fischer and Warburg for leucine. α-Amino-β-methylvaleric acid is a particularly refractory compound, since it was not resolved by the crystallisation of the salts of five different alkaloids with four of its derivatives.

Pope and Beck[39] show by the resolution of tetrahydro-*p*-toluquinaldine that another strong acid, the *d*-$\alpha\beta$-bromocamphorsulphonic acid of Armstrong and Lowry, may be added to the list of those available for the resolution of bases.

H. O Jones[40] has shown in the case of *d*- and *l*-camphoroximes and *d*- and *l*-camphor, using dextrorotatory turpentine oil and pure *l*-amyl bromide as solvents, that the solubility of optical isomerides in an optically active solvent is the same, and also that their rotatory powers are the same in active solvents.

Little progress has to be recorded in our knowledge of the spatial configuration of stereoisomerides, although a few important relationships have been established.

Fischer[41] has answered Rosanoff's[42] criticism of the method of representing optical isomerides by the prefixes *d*- and *l*- without reference to their rotatory power, which he proposed and which has been in general use for such a long time.

Rosanoff claims that Fischer's system is rendered useless and mis-

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[37] *Abstr.*, 1907, i, 314.

[38] *Ibid.*, 593.

[39] *Trans.*, 1907, **91**, 458.

[40] *Abstr.*, 1907, ii, 237.

[41] *Ibid.*, 148.

[42] *Ann. Report*, 1906, 193.

leading by the conversion of one compound, which is called *d*, into another compound, called *l*, as, for example, in the case of the transformation of *d*-glucuronic acid into *l*-xylose, and suggests various changes in the system of nomenclature.

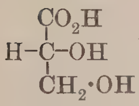
Fischer criticises these proposed changes adversely, but suggests that, to avoid confusion, *d′* and *l′* might be used when the prefixed letter does not indicate the sign of the rotation of the compound; thus glucose would be *d*-glucose, and lævulose *d′*-fructose.

Fischer and Jacobs[43] have fixed the spatial configuration of *d*-serine with reference to that of *d*-glyceric acid, the configuration of which had been referred to *d*-tartaric acid, and consequently to *d*-glucose, by Neuberg and Silbermann.

Later, Fischer and Raske[44] succeeded in converting *l*-serine into *d*-alanine, so that the configuration of the latter is therefore determined with reference to that of *d*-glucose, and, since *d*-alanine can be converted into *d*-lactic acid, the configuration of the latter is also determined; *l*-serine and *d*-alanine are the first of the amino-acids the configurations of which have been referred to that of *d*-glucose.

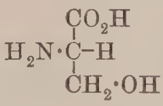
It is assumed that the reactions used are optically normal, and no "Walden inversion" has taken place.

The spatial configurations of these substances are represented thus:



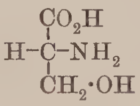
$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{H{-}C{-}OH} \\ | \\ \mathrm{CH_2{\cdot}OH} \end{array}$$

l-Glyceric acid (dextrorotatory)



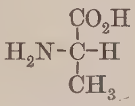
$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{H_2N{\cdot}C{-}H} \\ | \\ \mathrm{CH_2{\cdot}OH} \end{array}$$

l-Serine (natural)



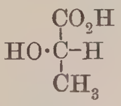
$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{H{-}C{-}NH_2} \\ | \\ \mathrm{CH_2{\cdot}OH} \end{array}$$

d-Serine



$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{H_2N{-}C{-}H} \\ | \\ \mathrm{CH_3} \end{array}$$

d-Alanine (natural)



$$\begin{array}{c} \mathrm{CO_2H} \\ | \\ \mathrm{HO{\cdot}C{-}H} \\ | \\ \mathrm{CH_3} \end{array}$$

d-Lactic acid

The changes which the guanidine compounds of the sugars undergo in aqueous solution have been very fully examined by Morrell and Bellars.[45] The guanidine compounds of dextrose, lævulose, and mannose show mutarotation in aqueous solution; the rotatory power finally becomes practically constant. The change is due to the interconversion of the three sugars brought about by the guanidine until equilibrium is attained; the changes are very similar to those caused by alkali hydroxides and investigated qualitatively by Lobry de Bruyn and van Ekenstein, but the action of guanidine differs from that of the alkali hydroxides in that the side reactions in which acids and coloured products are formed are much less pronounced.

Each change was followed quantitatively with the polarimeter, and the final state of equilibrium was determined by quantitative estimation of the sugars. The changes which take place are best represented by the following scheme:

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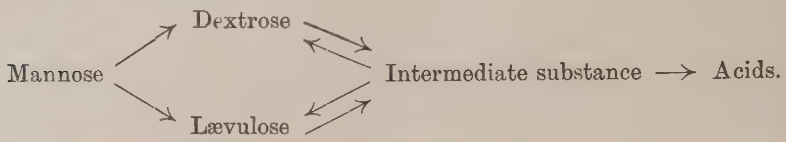
[43] *Abstr.*, 1907, i, 393.
[44] *Ibid.*, 900.
[45] *Trans.*, 1907, **91**, 1010.

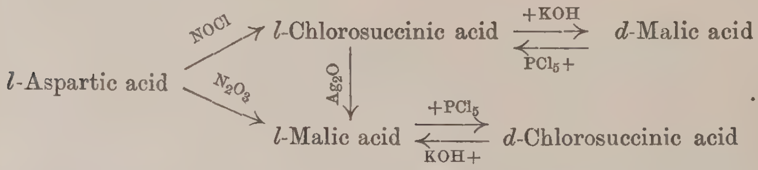


The velocity constant for the change of mannose into lævulose is 0·0005, and into dextrose 0·00036; the velocity constant for the transformation of dextrose into lævulose is 0·0015, and for the reverse change 0·0021, all referring to 37°. The velocity of formation of mannose from dextrose is very small, and the velocity of formation of acids is small.

McKenzie and Wren[46] have succeeded in effecting an asymmetric synthesis of tartaric acid; *l*-bornyl fumarate when oxidised yields a slightly lævorotatory acid; a much more decided result is obtained by using *l*-bornyl hydrogen fumarate. Similar results are obtained by using *l*-menthol; *d*-borneol yields a dextrorotatory tartaric acid.

The most remarkable observation made in the domain of stereochemistry, since the observations of Pasteur served to found this branch of chemistry, is that of Walden[47] on the curious change of configuration which takes place during the interconversions of malic and chlorosuccinic acids and is known as the "Walden inversion."

These observations on the changes which take place under the action of reagents may be summarised conveniently in the following scheme, in which are included also the observations of Tilden and Marshall[48] on aspartic acid:



The changes under the successive action of phosphorus pentachloride and silver oxide enable one to convert *d*-malic acid into *l*-malic acid or vice versa.

Walden came to the conclusion that the action of phosphorus pentachloride and caustic potash was "optically normal" or, in other words, that these reagents replaced the hydroxyl group by chlorine or vice versa without changing the spatial configuration of the groups around the asymmetric carbon atom, and that the action of silver oxide was optically abnormal. This conclusion is remarkable, since, from the known influence of caustic potash in causing racemisation, one would have expected this and not silver oxide to behave abnormally. Walden tried the effect of a large number of different metallic oxides and hydroxides, which he found, when arranged in order according to the amount of inversion caused by each, formed a series with caustic potash at one end and silver oxide at the other. Walden was unable to use the corresponding esters, since these were saponified by caustic potash and were hardly affected by silver oxide. Which of the two reagents, nitrosyl chloride or nitrous fumes, behaved abnormally was not settled.

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[46] *Trans.*, 1907, **91**, 1215.

[47] *Abstr.*, 1896, i, 205; 1898, i, 127, 178; 1899, ii, 538.

[48] *Trans.*, 1895, **67**, 494.

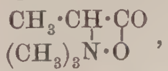
The problem practically remained as Walden left it until Fischer,[49] during the course of his study of amino-acids, observed the following instance of a "Walden inversion":

$$\begin{tikzcd}
d\text{-Alanine } (\alpha\text{-amino-propionic acid}) \arrow[r, "\text{NOBr}"] & l\text{-Bromopropionic acid} \arrow[d, "NH_3"] \\
l\text{-Bromopropionic acid.} \arrow[u, "NH_3"] & l\text{-Alanine.} \arrow[l, "\text{NOBr}"']
\end{tikzcd}$$

Similar observations were also made on leucine and on phenylalanine.

The reaction of ammonia with the halogen acids proceeds much more smoothly and easily than the action of caustic alkalis, and can be carried out by treatment with aqueous or liquid ammonia; further, the ester of the bromo-acid may be used instead of the acid. Some racemisation always occurs during the reactions.

The conclusion is drawn that the action of ammonia is optically normal, and this is supported by later experiments on an analogous reaction of trimethylamine,[50] which acts on d-α-bromopropionic acid to give lævorotatory trimethyl-α-propiobetaine,



$$\begin{array}{l} CH_3\cdot CH\cdot CO \\ (CH_3)_3N\cdot O \end{array},$$

identical with that obtained by the action of methyl iodide on d-alanine in alkaline solution.

The action of nitrosyl bromide on d-alanine ester proceeds smoothly, with the result that d-bromopropionic ester is formed. Similar results were obtained with d-leucine ester and with l-aspartic ester; hence it follows that the action of nitrosyl bromide on the acid must be optically abnormal.

Phosphorus pentachloride yields products having the same configuration when it acts on a hydroxy-acid and when it acts on the ester of the same acid; it is probable therefore that its action is optically normal, but further evidence on this point is desirable, and especially is it necessary to settle conclusively whether caustic potash or silver oxide is the abnormal reagent.

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[49] *Abstr.*, 1905, i, 692; 1906, i, 808. See also *ibid.*, 1907, i, 192.

[50] *Ibid.*, 1908, i, 80.

Since esters are not available, as stated above, on account of the hydrolysing action of caustic potash, a bromo-polypeptide, *α*-bromopropionylglycine, was used; this, when treated with silver oxide, yielded a syrup which, after hydrolysis with dilute acid, gave lactic acid. The following observations then prove that the action of silver oxide is optically abnormal as stated by Walden:

l-Bromopropionic acid $\xrightarrow{KOH}$ *l*-Lactic acid.
l-Bromopropionic acid $\xrightarrow{Ag_2O}$ *d*-Lactic „
l-*α*-Bromopropionylglycine $\xrightarrow[\text{and hydrolysis}]{Ag_2O}$ *l*-Lactic „

It is also clear that the "Walden inversion" is dependent on the presence of the carboxyl group, and, further, a comparison of these changes with the changes in configuration which sugars undergo under the influence of alkalis, and sugar acids under the influence of pyridine or quinoline, would appear to justify the conclusion that it is only an asymmetric carbon atom in the *α*-position to an electronegative group that can undergo this inversion. Several other cases of the "Walden inversion" are recorded in later papers on polypeptides.

As regards the mechanism of this inversion, Fischer is inclined to agree with Walden that the formation of intermediate products is responsible for the change. An additive product of aspartic ester and bromine has been found to have the formula $C_8H_{15}O_4\cdot NHBr,Br_2$; if a further additive product be formed from this compound and nitric oxide, from which the amino-group is eliminated and replaced by a bromine atom, a possible method in which the "Walden inversion" takes place can be imagined. If, in this additive compound, it be assumed that the bromine atom which is eventually to become attached to the asymmetric carbon atom is already within the sphere of influence of this carbon atom, then all that is necessary in order to effect a "Walden inversion" is that, when the amino-group is eliminated and replaced by bromine, the carboxyl group should slide into the position formerly occupied by the amino-group and that the bromine atom should take its place. A similar scheme might be conceived for the action of silver oxide, and it is probable that the presence of a carboxyl group determines the formation of these additive products.

The results of the further investigation of these changes will be awaited with considerable interest, since it is extremely probable that, through them, we shall acquire valuable information concerning the mechanism of some chemical reactions and the internal structure of chemical molecules.

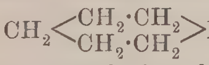
The problem of the origin of natural petroleum has again attracted attention, and valuable experimental evidence has been brought forward by Neuberg[51] and by Lewkowitsch and Pick[52] in support of the hypothesis of Engler and Hofer that mineral oils have an organic origin.

Neuberg[53] had shown that proteins on decomposition yield optically active fatty acids, and now shows that, by the action of heat on these acids, oils having all the characteristic properties of natural petroleum are produced. A mixture of oleic acid and *d*-valeric acid yielded an optically active petroleum when distilled or heated under pressure.

Lewkowitsch and Pick show that chaulmoogra oil, when distilled with zinc dust, yields an optically active petroleum, so that fats as well as proteins can give rise to optically active hydrocarbons.

In this connexion, it may be interesting to mention that Jones and Wootton[54] found that petroleum from Borneo, which contains large quantities of aromatic hydrocarbons, is lævorotatory, and that this activity is due both to the aromatic and to the other hydrocarbons present in the less volatile fractions.

Some contributions to our knowledge of phenomena attributed to steric hindrance have been made during the year.

Kaufler[55] suggests that the usual formulæ for polycyclic compounds, such as diphenyl, and for conjugated ring systems, such as naphthalene, should be replaced by space formulæ representing the manner in which the planes of the different rings are inclined to one another. A space formula for benzidine is given which, it is claimed, explains the difficulty experienced in diazotising the second amino-group, and simplifies the conception of the formation of benzidine from hydrazobenzene. This suggested formula does not, however, appear very probable, and the difficulty referred to by Kaufler does not exist. Scholtz and Wassermann[56] describe a number of cases in which piperidine derivatives,  $CH_2{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}N\cdot R$, are formed from αε-dibromopentane and *m*- or *p*-substituted aromatic amines, whereas *o*-substituted amines yield derivatives of pentamethylenediamine, $R\cdot NH\cdot[CH_2]_5\cdot NH\cdot R$.

Hans Meyer,[57] shows that, in the case of some esters of substituted cinchonic acids, the fact that methyl esters are often less stable than ethyl esters may outweigh the influence of steric hindrance, so that methyl esters in which steric hindrance is expected to occur can be hydrolysed more readily than ethyl esters, in which there is no steric hindrance.

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[51] *Abstr.*, 1907, i, 577, 997.

[52] *Ibid.*, 997.

[53] *Ibid.*, 1906, i, 923.

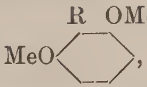
[54] *Trans.*, 1907, **91**, 1149.

[55] *Abstr.*, 1907, i, 307.

[56] *Ibid.*, 339.

[57] *Ibid.*, 342.

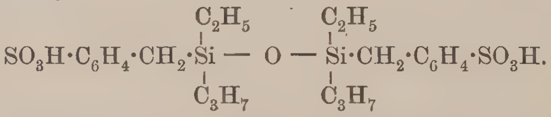
Kauffmann and Franck[58] describe a number of striking instances of total absence of, or greatly diminished velocity of, reactions involving the group R in resorcinol derivatives of the type:



whereas substitutions in the nucleus take place readily; the reactivity of the group R must therefore be greatly diminished by the steric hindrance of the two methoxyl groups.

It is gratifying to note that Kipping's persistent efforts to establish the ability of silicon to give rise to optical activity under the same conditions as carbon have been rewarded with success.[59] Great experimental difficulties have been encountered, since the silicon compounds examined so frequently behave in a quite unexpected way towards reagents, and also because they appear to be exceptionally difficult to resolve. Here one can only summarise the important facts which justify the conclusion that an optically active silicon compound has been prepared.

Phenylbenzylethylpropylsilicane, on treatment with sulphuric acid, yields benzene and a compound which is shown to be sulphobenzylethylpropylsilicyl oxide:



$$SO_3H\cdot C_6H_4\cdot CH_2\cdot \underset{C_3H_7}{\overset{C_2H_5}{Si}} - O - \underset{C_3H_7}{\overset{C_2H_5}{Si}}\cdot CH_2\cdot C_6H_4\cdot SO_3H.$$

Since two asymmetric silicon atoms are present, it is to be expected that the product formed would be a mixture of an externally compensated compound analogous to racemic acid and of an internally compensated compound analogous to mesotartaric acid; one only of these has been isolated, which is shown to be the *dl*- or externally compensated compound.

The salts of this acid with *l*-menthylamine, *l*-bornylamine, cinchonidine, strychnine, and *d*-methylhydrindamine were prepared and examined. In the case of the salt of the last-mentioned base only was there conclusive evidence of resolution into two components on recrystallisation. The two salts obtained have different melting points, but show practically the same rotatory power in solution, and yet the sodium salts of the acids prepared from them show small specific rotatory powers of 3·3° and −4·5° respectively. The less soluble salt yields the dextrorotatory sodium salt.

The enantiomorphous relationship of the acids contained in the two *d*-methylhydrindamine salts is proved by examining their behaviour towards *l*-methylhydrindamine. Each of the two salts was first converted into the ammonium salt, and this was treated with the hydrochloride of *l*-methylhydrindamine with the following results:

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[58] *Abstr.*, 1907, i, 1092.

[59] *Trans.*, 1907, 91, 209.

Less soluble *d*-methylhydrindamine salt, m. p. 205° ⟶
l-methylhydrindamine salt, m. p. 145°.
More soluble *d*-methylhydrindamine salt, m. p. 135° (slightly impure) ⟶
l-methylhydrindamine salt, m. p. 205°.

The enantiomorphous relationship of the acids is thus proved, not only by the opposite rotatory powers of their sodium salts, but also by their behaviour towards two enantiomorphously related bases, giving four salts enantiomorphously related in pairs, thus: *dBdA* and *lBlA*, melting at 205°, and *dBlA* and *lBdA*, melting at 145°.

In a later paper, the same author[60] describes the preparation of another compound containing an asymmetric silicon atom, benzylmethylethylpropylsilicane, which by treatment with chlorosulphonic acid is converted into a sulphonic acid. The salts of this acid with seven optically active bases have been examined, but hitherto no evidence of resolution has been obtained.

A number of papers dealing with the optical activity of quinquevalent nitrogen compounds have appeared. Our knowledge of the principles governing the isomerism of these compounds is gradually being extended, and these principles are shown to be analogous to those which apply to asymmetric carbon compounds.

The autoracemisation of optically active ammonium halide salts in chloroform solution, first observed by Pope and Harvey,[61] who suggested that it was due to partial dissociation of the salt into tertiary amine and alkyl halide, has again attracted attention. The phenomenon has been observed in the case of practically all the active nitrogen compounds which have been prepared; all these compounds contain an allyl or a benzyl group, or both.

Goldschmidt[62] does not consider that the evidence in favour of the hypothesis that dissociation is responsible for the racemisation is conclusive, and von Halban[63] points out that considerable decomposition occurs in a chloroform solution of phenylbenzylmethylallylammonium iodide. Wedekind,[64] however, shows that the decomposition in the case of the corresponding compound containing the *n*-propyl instead of the allyl group is but slight, and yet autoracemisation in this case also proceeds rapidly in chloroform solution.

The absence of extensive dissociation or decomposition in chloroform solutions of these salts was proved by the molecular weight determinations carried out by Barger[65] on two iodides containing the benzyl group attached to an asymmetric nitrogen atom, in which the value found for the molecular weight in chloroform was almost normal at first, but diminished slightly to a constant value on standing for a long time. The decomposition which occurs is therefore not extensive. The hypothesis that dissociation into tertiary amine and alkyl halide is responsible for the autoracemisation of these salts received strong support from the experiments of the present writer [66] on the α- and β-phenylbenzylmethyl-*l*-amylammonium iodides, in which it was found that both these iodides, one of which, α, was dextrorotatory and the other lævorotatory, gradually attained the same dextrorotatory power on standing in chloroform solution.

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[60] *Trans.*, 1907, **91**, 717.

[61] *Ibid.*, 1901, **91**, 828.

[62] *Ann. Report*, 1906, 197.

[63] *Abstr.*, 1907, ii, 246.

[64] *Ibid.*, 246.

[65] *Trans.*, 1904, **85**, 230.

Dissociation into alkyl halide and tertiary amine has now been shown to take place in the case of ammonium compounds containing one of the seven alkyl groups, methyl, ethyl, propyl (*n*- and *iso*), butyl (*n*- and *iso*), and *iso*amyl, as well as those containing the allyl or benzyl group by the experiments of Jones and Hill,[67] in which it is shown that the methyl group can replace each of the other groups in a quaternary ammonium salt when the latter is heated with methyl iodide.

Scholtz and Wassermann [68] have made further experiments proving the close analogy between the behaviour of the asymmetric carbon and nitrogen atoms. 2-Phenyl-6-methyl-1-ethylpiperidine, which contains two asymmetric carbon atoms, has been combined with benzyl iodide, thus making the nitrogen atom also asymmetric. Two of the four possible active forms of this compound have been used, and each of these gave two, α and β, forms of the ammonium iodide.

That weak acids, like tartaric acid, can be used for the resolution of optically active ammonium salts has been shown by Miss Homer [69] in the case of phenylbenzylmethyl*iso*propylammonium hydrogen tartrate. This method has been applied by Jones [70] to the examination of the phenylbenzylmethylethylammonium and phenylmethylethylallylammonium salts, which were found [71] to have rotatory powers very much smaller than those of the corresponding compounds containing homologous alkyl groups instead of the ethyl group. Wedekind and Fröhlich [72] had already re-examined the first compound and obtained a much higher value for its rotatory power than that previously assigned to it. It has now been found, by the resolution of the acid tartrate, that the phenylbenzylmethylethylammonium ion has a molecular rotatory power of about 288°, a value approximating to that of the corresponding *n*-propyl ion, 299°; in the same way, the phenylmethylethylallylammonium ion is found to have a much greater rotatory power than that previously assigned to it.

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[66] *Trans.*, 1905, **87**, 135.
[67] *Ibid.*, 1907, **91**, 2084.
[68] *Abstr.*, 1907, i, 340.
[69] *Ibid.*, 692.
[70] *Proc. Camb. Phil. Soc.*, 1907, **14**, 376.
[71] Thomas and Jones, *Trans.*, 1906, **89**, 280.
[72] *Ann. Report*, 1906, 197; *Abstr.*, 1907, i, 122.

Fröhlich and Wedekind[73] have resolved phenylbenzylmethyl-*n*-butylammonium *d*-camphorsulphonate, and found that the molecular rotatory power of the ion is $-254°$, which is lower than that of the corresponding *iso*butyl compound, namely, 323°; the relation of the two butyl compounds is therefore similar to that of the normal and *iso*propyl compounds of the same series ($[M]_D$ 299° and 398° respectively).

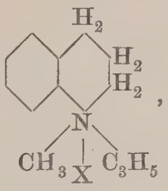
The iodide of the *n*-butyl compound has a molecular rotatory power of $-319{\cdot}6°$ in alcohol and $-346{\cdot}1°$ in chloroform solution; in chloroform solution, autoracemisation of the iodide takes place much less rapidly than in the case of the corresponding *iso*butyl compound.

Wedekind and Fröhlich[74] have also examined and resolved compounds containing the anisole and phenetole groups. *p*-Ethoxyphenylbenzylmethylallylammonium *d*-camphorsulphonate was partially resolved, and yielded an iodide with a specific rotatory power of $+6{\cdot}39°$ in chloroform.

The corresponding *p*-ethoxy-compound was also resolved by means of its camphorsulphonate, and the ion was found to have a molecular rotatory power of $-11{\cdot}1°$, and the iodide in chloroform solution had a specific rotatory power of $-6{\cdot}65°$. The low value of the rotatory power of these compounds as compared with the corresponding phenyl compounds ($[M]_D$ for ion = 166°, and $[\alpha]_D$ for iodide in chloroform = 55·4°)[75] is very remarkable.

p-Ethoxyphenylbenzylmethylallylammonium iodide has also been prepared in three different ways, namely, by the addition of methyl, allyl, or benzyl iodide to the corresponding tertiary amine. Each reaction proceeds normally and the three products are identical. The conclusion that no stereoisomerides of inactive asymmetric nitrogen compounds can be formed in this way is further substantiated by the results of these experiments.

The isolation of optically active compounds owing their activity to the asymmetry of a single nitrogen atom which forms part of a closed ring has at last been effected by Buckney,[76] the compounds being allylkairolinium salts of the formula:



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[73] *Abstr.*, 1907, i, 512.

[74] *Ibid.*, 409, 410.

[75] Pope and Harvey, *Trans.*, 1901, **79**, 828.

[76] *Abstr.*, 1907, i, 722.

in which the asymmetric nitrogen forms part of a tetrahydroquinoline molecule. The same compound has also been resolved by E. and O. Wedekind[77] in the same way, namely, by fractional crystallisation of the *d*-bromocamphorsulphonate. The salt *lBdA* is the less soluble, and gives the molecular rotatory power of 196° ($[M]_D$ for acid ion, 270°); the *dBdA* salt does not appear to have been obtained in a pure state, although the last-named authors obtained a higher value for the rotatory power of the basic ion in this salt than that obtained from the *lBdA* salt.

The iodide recovered from the *lBdA* salt was found to be optically active ($[M]_D$ $-65°$), and to undergo autoracemisation very readily.

Buckney and Jones[78] describe the examination of a number of quinoline and tetrahydroquinoline derivatives which, according to theory, should be capable of giving rise to optical activity; in one case only, namely, the allylkairolinium compounds mentioned above, was conclusive evidence of optical activity obtained. Altogether in this paper, and in a former paper,[79] eight tetrahydroquinoline derivatives containing an asymmetric nitrogen atom have been examined and only one resolved; there seems to be no assignable reason for the fact that much greater difficulty is experienced in resolving these cyclic nitrogen compounds than the ordinary substituted ammonium compounds of which so many have now been resolved into their optically active components.

H. O. Jones.

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[77] *Abstr.*, 1907, i, 1073.

[78] *Trans.*, 1907, **91**, 1821.

[79] *Ibid.*, 1903, **83**, 1415.

ANALYTICAL CHEMISTRY.

The fact that the function of the writer of this Report must, from the nature of the subject, be that of a judicious reporter rather than of a reviewer has been insisted upon in previous Annual Reports, and the difficulty of treating the subject of the progress in Analytical Chemistry in the form of a connected narrative has been pointed out. The field to be covered is a very large and ever-increasing one, and from some inquiries which he has made, the author is led to believe that the arrangement of the subject-matter, which he has adopted in past years, is perhaps the clearest and most convenient one for the reader. The work of the year will therefore be dealt with as before, under the following headings:

(1) Inorganic Chemistry, including electrochemical methods.
(2) Organic Analysis.
(3) Analysis of Foods and Drugs.
(4) Toxicological Analysis.
(5) Apparatus.

The above subdivision of the subject is, of course, to some extent an arbitrary one, but it appears to permit of a more methodical treatment than any other with which the writer is acquainted.

Inorganic Chemistry.

In connexion with the qualitative section of this branch, there are but few communications which merit special reference.

The detection of ferrocyanides, ferricyanides, and thiocyanates in the presence of one another is not always easy, and an apparently useful method which appears to be characterised by certainty and delicacy has been proposed for this purpose by Browning and Palmer.[1] This depends on the fact that the ferrocyanides can be separated from the ferricyanides and from the thiocyanates by precipitation with a salt of thorium, whilst the ferricyanides can in turn be separated from the thiocyanates by precipitation with a salt of cadmium. The main difficulty is in connexion with filtration, but the method has given good results in the writer's hands.

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[1] *Abstr.*, 1907, ii, 724.

In mineral analyses, it is frequently necessary to test silica precipitates for the presence of small quantities of oxide of titanium, and Knecht[2] has described a method based on the reduction of the titanium oxide and the decolorising effect of the resulting solution when added to a solution of Rochelle salt, coloured slightly with indigotin, or, better, with methylene-blue.

The detection of sulphites in the presence of thiosulphates and thionates presents some difficulty, and a method proposed by Votoček[3] seems likely to be useful. It is based on the fact that, whilst normal sulphites destroy the colours of solutions of certain triphenylmethane dyes, thiosulphates and di-, tri-, and tetrathionates are without effect. The most suitable reagent consists of a mixture of a solution of magenta with one of malachite-green, and the author states that as little as 0·00006 gram of sulphurous acid (as normal sulphite) can be detected.

For the detection of traces of moisture in gases or liquids, W. Biltz[4] makes use of potassium lead iodide, an almost colourless salt, which is readily decomposed by traces of water with separation of yellow lead iodide. Test papers may be easily prepared with this reagent, and constitute a convenient method of applying the reaction. Ehrenfeld[5] shows that the red precipitate sometimes obtained on acidifying the ammonium carbonate solution, which has been used for the separation of arsenic and tin in the ordinary process of analysis, consists of arsenic disulphide, the reduction of the higher sulphides being readily effected by stannous chloride in acid solution.

Pozzi-Escot[6] recommends for the detection of traces of nickel the use of ammonium molybdate, which gives a green, crystalline precipitate even in the presence of a considerable excess of cobalt. Tschugaeff,[7] however, points out that this test is far less sensitive than that based on the use of dimethylglyoxime, which is said to be capable of detecting as little as one part of nickel in two million parts of water.

The ionisation theory, which was, I believe, first put forward by Ostwald to explain the colour changes manifested by indicators, has been very generally accepted as correct, notwithstanding an important paper published some years ago by Stieglitz,[8] who suggested what he termed the "chromophoric" theory, pointing out that it was more probable, for example, that phenolphthalein, in its colourless solution, has the constitution of a lactone, whilst its salts are derivatives of a carboxylic acid containing the chromophoric quinonoid complex $:C_6H_4:O$. Following up his work on the colorimetric measurement of affinity, Salm, in conjunction with Friedenthal, has recently published a paper[9] on this subject, in which he adduces some evidence for the belief that the colour changes of indicators are, in many cases, due rather to intramolecular change than to ionisation. In this connexion, it may be mentioned that Knowles[10] recommends alizarin-red I.W.S. (alizarinmonosulphonic acid) for use in alkalimetry instead of methyl-orange, over which it appears to possess some advantages, and that O. Stark[11] states that excellent results may be obtained with 3-amino-2-methylquinoline as an indicator, especially in substitution for methyl-orange in the titration of ammonia. As a standard substance for use in alkalimetry and acidimetry, Phelps and Hubbard[12] recommend succinic acid, obtained by the hydrolysis of ethyl succinate.

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[2] *Abstr.*, 1907, ii, 654.
[3] *Ibid.*, 195.
[4] *Ibid.*, 574.
[5] *Ibid.*, 949.
[6] *Ibid.*, 818.
[7] *Ibid.*, 989.
[8] *Ibid.*,1904, ii, 17.

Ronchèse[13] describes an ingenious method for the estimation of ammonia, based on the reaction of formaldehyde with ammonium salts, whereby hexamethylenetetramine is formed, and, if the formaldehyde is in sufficient excess, the whole of the acid of the ammonium salt is liberated, and may be titrated with standard alkali.

In former reports, reference has been made to the estimation of sulphuric acid by Raschig's benzidine method, and, as this method is capable of giving good results and may occasionally be of use, it would seem desirable to direct attention to a paper by Friedheim and Nydegger[14] on this subject. The authors have fully investigated the most favourable conditions for precipitation, and give full particulars in regard to the solubility correction.

The "nitron" method for the gravimetric estimation of nitric acid has been submitted to a detailed and critical study by S. W. Collins,[15] who finds that good results can be obtained both with simple and mixed pure nitrates and in commercial products, such as natural waters and nitrate-containing fertilisers. In view of the expense of the "nitron," it is satisfactory to note that the author has succeeded in devising a process for the recovery of the base.

Last year, Jannasch and Heimann[16] succeeded in quantitatively volatilising phosphoric acid from its salts by making an intimate mixture of the phosphate with carbon, and distilling off the phosphoric acid in a stream of chlorine. This method, although it gave good results with ammonium hydrogen phosphate and with

[9] *Abstr.*, 1907, ii, 389.
[10] *Ibid.*, 389.
[11] *Ibid.*, i, 974.
[12] *Ibid.*, ii, 297.
[13] *Ibid.*, 651.
[14] *Ibid.*, 196.
[15] *Ibid.*, 907.
[16] *Ibid.*, 1906, ii, 745.

ammonium magnesium phosphate, was somewhat clumsy and difficult to carry out. Jannasch and Jilke[17] have now improved on this, in that the phosphoric acid is distilled off by heating strongly in a stream of chlorine mixed with the vapour of carbon tetrachloride. The results given for ammonium phosphate and for magnesium phosphate are very good, and the method is one which might, in certain cases, be usefully employed in mineral analysis. The time required for the carrying out of the process (between four and five hours for the vaporisation of an amount of phosphoric acid equivalent to about 0·3 gram of magnesium pyrophosphate) would, however, constitute a drawback from the point of view of practical laboratory procedure.

The quantitative separation of the halogens constitutes a very important analytical problem, and one to the solution of which a great many chemists have at various times devoted themselves. The principle underlying almost all existing methods is that of differential oxidation, and, as the "oxidation potential" of all the oxidising agents recommended is, with one exception, higher than that of an aqueous solution of chlorine, it follows that good results can only be obtained by accurately interrupting the process when the whole of the bromine has been distilled over, and by paying minute attention to the experimental conditions, especially to the degree of acidity and concentration. Iodic acid constitutes the single exception referred to above, and was originally proposed for the separation of bromine and chlorine by Bugarszky.[18] This substance has an "oxidation potential" which lies between that of chlorine and that of bromine, and, consequently, it is well suited for the separation of these two halogens. The method, which does not appear to be so widely known as it should be, has been submitted to a further study by Andrews,[19] who has suggested certain improvements in the procedure, and has shown, not only that accurate results can be obtained in the separation of bromides and chlorides, but that the method is applicable to the estimation of chlorine in crude bromine. For the estimation of cyanogen in slightly dissociated salts, such as mercuric cyanide, mercuric cyanonitrate, and mercuric cyanochloride, Borelli[20] has proposed a method in which the cyanogen is obtained in the form of sodium cyanide by treatment with aluminium powder in a solution rendered strongly alkaline with sodium hydroxide. The results appear to be good, and the process, which is also applicable to the determination of cyanogen in complex iron cyanides, is more rapid of execution than that of Rose. A good many methods have at various times been proposed for the analysis of mixtures of thiocyanates and chlorides, or bromides, and Rosanoff and Hill[21] have studied and criticised some of these, and have devised a method which appears to be both simple and rapid of execution. This depends on the oxidation of the thiocyanate to hydrocyanic acid by means of nitric acid, and is similar to one proposed years ago by Volhard, but differs from that in that the solution is not rendered alkaline, a treatment which, according to Rosanoff and Hill, causes the re-formation of some thiocyanate.

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[17] *Abstr.*, 1907, ii, 864.

[18] *Ibid.*, 1896, ii, 216.

[19] *Ibid.*, 1907, ii, 503.

[20] *Ibid.*, 825.

The separation of tellurium from certain heavy metals and its accurate estimation has occupied the attention of Brauner and Kuzma,[22] who show that, when tellurium in the presence of copper, bismuth, and antimony is precipitated by means of sulphur dioxide, appreciable quantities of the associated metals are carried down, and that this is especially the case with copper. In order to overcome this difficulty, the authors recommend the oxidation of the tellurium to telluric acid by means of ammonium persulphate, and the subsequent precipitation of the heavy metals with hydrogen sulphide. The tellurium can then be estimated by reduction with hydrochloric acid and sulphur dioxide. Incidentally, attention is called to the interesting fact that, when solutions containing both copper and tellurium are oxidised with the persulphate, an intense red coloration is observed, which the authors attribute to the formation of a derivative of cupric acid.

Hinrichsen[23] calls attention to the great difficulty there is in completely removing the hydrofluoric acid when that substance has been used in conjunction with sulphuric acid for the decomposition of silicates. He points out that, when ammonia is subsequently added for the purpose of precipitating the iron and aluminium, a double fluoride of ammonium and aluminium is formed, which is soluble in hot water, and he states that this behaviour may be the cause of introducing a very serious error into the aluminium estimation. This paper deserves the attention of all who are interested in mineral analysis. The estimation of iron, aluminium, and titanium, when present together, is a problem of very frequent occurrence in mineral analysis, and two papers dealing with this subject will be read with interest. One by Gallo[24] deals especially with the volumetric estimation of the titanium by titration with a solution of ferric alum, whilst in the other, by Magri and Ercolini,[25] a method for the electrolytic separation of the iron is described.

In this connexion, attention may be directed to a paper by Gooch and Newton,[26] who show that iron may be determined by titration with permanganate in the presence of titanium if some bismuth oxide is added to the reduced solution. This appears to have the effect of oxidising the titanium without affecting the ferrous salt, so that the latter may be directly titrated after filtration. Inasmuch as the authors specially recommend the use of amalgamated zinc for the reduction of the iron, the writer of this Report may perhaps be permitted once again to direct the attention of analysts to the great advantage of using charged palladium for that purpose. If the metal is fully charged, reduction is readily brought about, and there is obviously nothing to interfere with the sharpness of the end reaction with the indicator. The quantitative separation of zinc and cadmium by means of hydrogen sulphide is, as is well known, somewhat troublesome, inasmuch as the acidity limits within which such separation can be effected are very narrow, and in any case several precipitations are usually necessary. Fox [27] has shown that trichloroacetic acid may be advantageously substituted for the mineral acids usually employed in this separation, and that, unless the amount of zinc present is large in relation to that of the cadmium, a single precipitation is sufficient. A critical paper by Funk,[28] dealing with a kindred subject, namely, the separation of zinc from nickel, cobalt, iron, and manganese by means of hydrogen sulphide, is worthy of study, in view of the well-known difficulties attaching to the problem. The author recommends either precipitation from a solution containing formate or Treadwell's process, in which the precipitation is effected in the presence of an excess of an alkaline chloride or sulphate.

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[21] *Abstr.*, 1907, ii, 984.
[22] *Ibid.*, 716.
[23] *Ibid.*, 506.
[24] *Ibid.*, 402.
[25] *Ibid.*, 400.
[26] *Ibid.*, 507.

Glixelli [29] contributes a very interesting communication dealing with the theory of the action of hydrogen sulphide on zinc salts, and shows that, contrary to the generally accepted view, the reaction $ZnSO_4 + H_2S = ZnS + H_2SO_4$ is not a reversible one, but that false equilibria occur in acid solutions which are sometimes very persistent, and which can be upset, and precipitation hastened, by the presence of zinc, cadmium, or copper sulphides. The author is of opinion that the separation of zinc from nickel and cobalt in acid solutions by means of hydrogen sulphide does not depend on the difference in the equilibrium conditions, but on the induction periods.

There is still considerable room for investigation in connexion with the methods for estimating and separating many of the rare elements, and the results of such investigations are always welcome. This is the case with a paper by Paal and Amberger,[30] who have devoted a good deal of attention to the analytical chemistry of osmium. Although this rare element is of some technical importance, the methods recommended for its estimation do not appear to have been well worked out, and leave much to be desired in point of definiteness and accuracy. Of these, perhaps the most widely known is that in which the osmium is separated as Frémy's osmyldiammine chloride from alkaline osmate solutions. The above-mentioned authors have now shown that this method is very unsatisfactory, and have suggested several processes which will doubtless be carefully tested by those analysts who are actively interested in the analytical chemistry of the platinum metals. In this connexion, it may be noted that Makowka [31] has shown that osmium is completely separated from acid solutions by acetylene, and he also states that palladium in acid solution may be precipitated and separated from platinum and iridium by means of the same reagent. Those interested in this method may also be referred to two papers on the same subject by Erdmann and Makowka.[32]

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[27] *Trans.*, 1907, **91**, 964.

[28] *Abstr.*, 1907, ii, 398.

[29] *Ibid.*, 868.

[30] *Ibid.*, 404.

Dittrich and Freund [32a] have studied the separation of thorium, titanium, and zirconium from iron, and have devised a new method for separating titanium from zirconium. This consists in adding a dilute and faintly acid solution containing these elements to a boiling solution of ammonium salicylate. Zirconium salicylate is precipitated, the titanium remaining in solution. Small quantities of the latter element may be carried down with the zirconium, but complete separation may in such cases be effected by a second precipitation.

As an interesting example of the manner in which organic compounds are being pressed into the service of analytical chemistry, mention may be made of the use of dicyanodiamide sulphate as a precipitant for nickel. This substance, the use of which had previously been suggested for the detection of nickel, has now been applied by Grossmann and Schück [33] to its estimation. The dicyanodiamide precipitate may be converted into nickel sulphate, or apparently more accurate results are obtained by drying at 115° and weighing, the precipitate then having the composition

$$Ni(C_2H_5ON_4)_2.$$

Cobalt in the tervalent condition and zinc are not precipitated, and the method may be used for the separation of nickel from iron and from aluminium. Similarly, Brunck [34] has employed dimethylglyoxime, which had previously been suggested as a test for nickel, for the estimation of that metal, and its separation from certain other metals, such as zinc, manganese, iron, aluminium, and chromium. The results appear to be good, and the method is rapid, but the costliness of the reagent must tend considerably to restrict its use.

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[31] *Abstr.*, 1907, ii, 403.

[32] *Ibid.*, 399, 403.

[32a] *Ibid.*, 1908, ii, 134.

[33] *Ibid.*, 1907, ii, 582, 819.

[34] *Ibid.*, 582, 989.

Although there is little that is new in a paper by Kolb and Feldhofen,[35] these authors have done good service in calling attention to the fact that hydrogen peroxide may, under suitable conditions, be used for the purpose of reducing mercuric salts to the mercurous state. The best conditions for obtaining the mercurous chloride prior to its estimation by Hempel's well-known iodine method are given.

The detection of very small quantities of mercury in explosives has recently become a matter of some practical importance, owing to the marked manner in which minute quantities of mercuric chloride affect the Abel heat test. A satisfactory spectroscopical method for this purpose was devised by the late Dr. Dupré, and, in a recent paper, Hargreaves and Rowe[36] have described an electrolytic process, the mercury being deposited on a gold foil cathode, from which it can be obtained by sublimation in the form of globules for microscopical identification.

The "comparison of mirrors" method for the estimation of minute traces of arsenic, which was first suggested by Sanger, has been extended by that author and Gibson[37] to the estimation of very small amounts of antimony. It has been found that, when quantities less than 0·1 milligram of that element are added to the reduction flask under the conditions laid down by the authors, the whole is evolved as hydride. The test results are good. The Gutzeit, although distinctly inferior for most purposes to the Marsh-Berzelius method, has its uses, and Sanger and Black[38] have dealt at considerable length with the former process, and have made a detailed study of the conditions which must be observed if the greatest degree of sensitiveness and accuracy is to be obtained. Robertson and Napper[39] have devised a method for the estimation of small quantities of nitrogen peroxide which is specially applicable to the examination of the gaseous products of the decomposition of guncotton and other explosives. This is based on a comparison of the absorption spectrum of the gas under observation with that of a standard gaseous mixture, the spectrum of nitrogen peroxide being, as is well known, very characteristic, and altering markedly with the concentration.

Electrolytic Methods.

A good deal of very useful work has been done during the year in the study of electrochemical methods of analysis.

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[35] *Abstr.*, 1908, ii, 69.

[36] *J. Soc. Chem. Ind.*, 1907, **26**, 813.

[37] *Abstr.*, 1907, ii, 654.

[38] *Ibid.*, 1908, ii, 65.

[39] *Trans.*, 1907, **91**, 761.

Dormaar[40] has investigated the cause of the high results which are frequently obtained in the electrolytic estimation of antimony, and finds that, whilst they are partly due, as has usually been supposed, to the inclusion of sulphur compounds in the precipitate, they are chiefly due to oxidation changes inherent in the electrolytic process itself. The same conclusion has been arrived at by Foerster and Wolf,[41] who have identified antimony oxide as well as sulphur in the precipitated antimony. Foerster, Blankenberg, Brunner, Lee, and Römmler have made a detailed study of the influence of temperature on the electrolytic deposition of various metals, and some of their results are of importance. Thus it has been observed that, whilst at the ordinary temperature the decomposition potentials of zinc and nickel are so near to one another that electrolytic separation is impossible, the difference is so greatly increased at higher temperatures that a satisfactory separation can be effected. Other advantages appear to result in special cases from working at elevated temperatures.

The advantages of employing rotating electrodes are now well recognised. With these, it is possible to work with much higher current densities, whilst the time required for the deposition of the metal to be determined is very much shortened, and the deposit is, moreover, frequently obtained in a better form for weighing. A very important paper, and one embodying a considerable amount of very useful work, has been published by H. J. S. Sand,[42] who describes the results he has obtained working with rotating electrodes and employing graded potential. The test results are, as a rule, very good, and the electrolytic separation of no fewer than seven metals in one solution must surely constitute a record. Miss Langness[43] also details the results she has obtained in a number of estimations and separations when working with a rotating anode, and the paper is one which may be read with advantage. From the point of view of analytical chemistry, perhaps the most important, and certainly the most useful, electrochemical investigations are those undertaken with the object of ascertaining the precise working conditions necessary for the accurate separation of commonly associated metals. The above-mentioned papers afford instances of this class of communication, and, as another example, attention may be drawn to a paper by Miss Kollock and E. F. Smith,[44] who have determined the time necessary for the complete deposition of a number of metals when varying amounts of sulphuric acid were present in the electrolyte, a mercury cathode and a rotating anode being employed. Results are also given showing the best experimental conditions for effecting certain separations. Another interesting communication is that of Hildebrand,[45] who shows that the negative radicles in such compounds as the carbonates, thiocyanates, and ferrocyanides of the alkali and alkaline earth metals may be estimated by employing a cell with a mercury cathode and a rotating silvered platinum anode. This work has been extended by McCutcheon, jun.,[46] by Lukens and E. F. Smith,[47] and by McCutcheon, jun., and E. F. Smith.[48] These authors have observed that, when solutions of metallic chlorides are electrolysed according to Hildebrand's method, the metals are capable of being divided into two classes, according to the behaviour of the amalgams formed. Thus the amalgams of lithium, sodium, potassium, calcium (see below), strontium, and barium decompose in the outer, or cathode, compartment with formation of the corresponding hydroxides, whilst the amalgams of magnesium, aluminium, and the heavy metals are decomposed with formation of the corresponding hydroxides in the inner, or anode, compartment. It was therefore possible in this way to carry out electrolytically a number of interesting separations. It is noteworthy that in the electrolysis of solutions containing both magnesium and calcium chlorides, none of the latter metal passes into the outer compartment, as is the case when calcium chloride alone is used. It would appear therefore that on this behaviour an interesting method might be based for the electrolytic separation of calcium from barium and strontium. In order to obviate the necessity for using a motor for the purpose of rotating the electrodes, Frary[49] has adopted the device of causing the electrolyte itself to rotate by placing it within a solenoid, through which the current used for the electrolysis passes. The conditions affecting the accuracy of the results obtained in the electrolytic estimation of lead have been somewhat exhaustively studied by Vortmann,[50] who shows that good results are not so easily obtained as is often imagined, and that there are a good many substances which interfere, and in the presence of which special treatment becomes necessary. It is well known that the ease with which many oxidation and reduction changes can be effected depends very greatly on the nature of the metal of which the electrode concerned is constructed. This phenomenon, usually referred to as "supertension" or "over-voltage," has been ascribed by Tafel, Caspari, and others to the pressure at which the hydrogen and oxygen respectively are set free at the surfaces. Kaufler,[51] however, contends that it is largely, if not entirely, due to local heating of the electrodes, and has shown that a low "potential" metal, such as platinum, is capable of bringing about changes which can usually be effected only by high "potential" metals if suitable means are taken to heat the electrode sufficiently.

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[40] *Abstr.*, 1907, ii, 200. [41] *Ibid.*, 508. [42] *Trans.*, 1907, **91**, 373.
[43] *Abstr.*, 1907, ii, 585. [44] *Ibid.*, 719.

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[45] *Abstr.*, 1907, ii, 574.
[46] *Ibid.*, 988.
[47] *Ibid.*, 988.
[48] *Ibid.*, 988.
[49] *Ibid.*, 649.
[50] *Ibid.*, 302.
[51] *Ibid.*, 924.

Organic Analysis.

Reactions (chiefly dependent on colour changes) of more or less complicated organic substances, even when characteristic, are, as a rule, of very little general interest, but reference may perhaps be made to communications dealing with some analytical reactions of veronal (diethylmalonylcarbamide) by Lemaire,[52] and of maretine by the same author,[53] of adrenaline by Krull,[54] of vesipirin (phenylacetosalicylate) by Zernik,[55] and of antipyrine by Steensma,[56] as these substances are of therapeutic importance. A simple reaction of adrenaline, which is said to be characteristic, is also described by Gunn and Harrison.[57] Molinari[58] has investigated the use of ozone as a reagent for the study of the unsaturatedness of organic compounds. The author finds that unsaturated compounds, whether aliphatic or aromatic, containing double bonds combine readily with ozone, whilst aliphatic compounds containing triple bonds, although uniting directly with a large proportion of iodine, do not absorb ozone. For the detection of small quantities of hydrocyanic acid, Thiéry[59] recommends the use of test papers, moistened first with a dilute solution of copper sulphate, and then with an alkaline solution of phthalophenone. In the presence of hydrocyanic acid, a fairly permanent rose-red coloration is produced, and the test is said to be capable of detecting the presence of as little as one part of hydrocyanic acid in two million parts. The separation of dyestuffs in mixtures is often a matter of considerable difficulty, and the suggestion of E. Lehmann[60] that advantage may sometimes be taken of the different rates of diffusion into jellies is noteworthy. With a mixture of eosin and tartrazin, for instance, sufficient separation could be effected to permit of certain identification. A very comprehensive paper dealing with the identification of dyestuffs on vegetable fibres by Green, Yeoman, Jones, Stephens, and Haley[61] cannot fail to be of great assistance, not only to colour chemists, but also to those whose incursions into this difficult field of analysis are of less frequent occurrence.

W. E. Marshall[62] confirms the value of the *p*-dimethylaminobenzaldehyde test for indole, and shows that it is capable of distinguishing that substance from others giving very similar general reactions, and that it can, moreover, be employed quantitatively as a chlorimetric method.

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[52] *Rep. Pharm.*, 1907, **19**, 104.
[53] *Ibid.*, 49.
[54] *Abstr.*, 1907, ii, 316.
[55] *Apoth. Zeit.*, 1907, **22**, 152.
[56] *Abstr.*, 1907, ii, 995.
[57] *Ibid.*, 591.
[58] *Ibid.*, i, 1039.
[59] *Ibid.*, ii, 408.
[60] *Ibid.*, 234.
[61] *J. Soc. Dyers*, 1907, **23**, 252.
[62] *Abstr.*, 1907, ii, 995.

As I have already referred in previous reports [63] to Dennstedt's method of elementary analysis, it is well that attention should be called to a paper by Baumert,[64] who describes certain modifications which he has introduced into this combustion process. In this connexion, reference may also be made to two papers dealing with the relative advantages of platinum and palladium as contact substances in organic analysis, the one by A. Jacobsen and Landesen,[65] and the other by Dennstedt.[66] The latter author is of opinion that platinum is for several reasons to be preferred to palladium, and points out that, although both these substances give better results with methane than oxide of copper, neither is capable of bringing about the complete oxidation of that gas. Quite a number of new methods for the estimation of halogens in organic compounds has been suggested during recent years, some of which are both rapid and exact, and the analyst is no longer compelled to choose between the somewhat dangerous method of Carius and the troublesome lime-combustion process. Chablay, for instance,[67] describes a convenient and apparently accurate method, in which advantage is taken of the fact that halogen-containing organic compounds react with sodammonium with quantitative formation of the sodium halide. For the estimation of phosphorus and sulphur in organic compounds by the fusion method, Stutzer [68] recommends the use of basic calcium nitrate, since this substance not only supplies the alkali necessary to prevent any loss of the elements in question, but also melts below 100°, and does not exhibit any tendency to detonate or spirt. For the estimation of hydrogen in a very large number of organic and inorganic compounds, Lidoff [69] recommends a volumetric method involving the ignition of the compound with magnesium or aluminium powder. The results appear to be good, and sulphur, nitrogen, and the halogens may be determined in the ignited residue by the usual methods. It will be remembered that a few years ago, Hibbert and Sudborough [70] showed that, by observing certain precautions, Grignard's magnesium alkyl halide method, which had been proposed by Tschugaeff for the detection of hydroxyl groups, might be made quantitative, and they published a number of results in support of this contention. This method has now been further examined at Tschugaeff's request by Zerewitinoff,[71] who has obtained very satisfactory results with a considerable number of organic compounds, differing widely in their chemical characters, and there can be no doubt that the method is a very useful one. The writer of this Report, in conjunction with Whitteridge,[72] has devised a method for the estimation of tartaric acid which may be usefully employed in many cases in which the ordinary potassium hydrogen tartrate method is, for various reasons, inapplicable. The tartaric acid is precipitated as a basic bismuth tartrate, which is dissolved in acid, and determined volumetrically by titration with permanganate. Lasserre[73] calls attention to a convenient method of separating formic and acetic acids, on the one hand, from butyric and valeric acids, on the other, based on the fact that the two last-mentioned acids can be extracted from their aqueous solutions by means of benzene or toluene. Propionic acid cannot be separated in this way, as it is equally soluble in benzene, toluene, and water. If, as appears to be the case, this separation is sharp, the method is likely to be much used. In previous Reports,[74] attention was called to the employment by Knecht, and subsequently by others, of titanium trichloride as a reducing agent for use in chemical analysis. It has an even more powerful reducing action than stannous chloride, and may be used for the estimation, not only of such substances as ferric iron, but also for the determination of organic nitro-compounds, such as trinitrocresol, dinitrobenzene, and dinitronaphthalene, as well as of azo-dyes, such as benzopurpurin. In a recent paper, Knecht and Miss Hibbert[75] describe the results of further work in this direction, and show that in many cases where direct titration with the titanium trichloride gives inaccurate results, good results can be obtained by adding an excess and titrating back with a standard ferric solution. The authors also recommend the use of this reagent for the evaluation of commercial hyposulphites and for the estimation of dissolved oxygen in water. One advantage of the titanium over the permanganate method in the latter estimation is that it is not affected by any organic matters which may be present. This paper is one which will well repay study, especially by those chemists who are interested in the analysis of organic dyestuffs. In my previous Report,[76] I called attention to a paper by Valenta, in which he recommended the use of methyl sulphate for the purpose of distinguishing between aromatic and paraffin hydrocarbons and separating them. This method has since been studied by Graeffe,[77] who has shown that aliphatic hydrocarbons are not by any means completely insoluble in methyl sulphate, and that in separations their solubility is often still further increased by the presence of the dissolved coal-tar hydrocarbons. Notwithstanding this, the method is, in certain cases, capable of being usefully employed.

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[63] *Ann. Report*, 1905, 195 ; 1906, 211.

[64] *Abstr.*, 1907, ii, 909.

[65] *Ibid.*, 718.

[66] *Ibid.*, 909.

[67] *Ibid.*, 195.

[68] *Ibid.*, 906.

[69] *Ibid.*, 574.

[70] *Trans.*, 1904, **85**, 933.

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[71] *Abstr.*, 1907, ii, 509.

[72] *Ibid.*, 513.

[73] *Ibid.*, 991.

[74] *Ann. Report*, 1905, 195; 1906, 207.

[75] *Abstr.*, 1907, ii, 907.

[76] *Ann. Report*, 1906, 214.

[77] *Chem. rev. Fett.-Harz.-Ind.*, 1907, 14, 112.

Of all the problems in organic analytical chemistry, perhaps one of the most difficult consists in the quantitative analysis of certain complex artificial carbohydrate mixtures. Indirect methods have almost invariably to be employed, and errors in the estimation of some of the substances present, although not serious in themselves, are sometimes apt to become additive, and to fall with very serious effect upon the estimation of some one constituent. During recent years, there has been an increasing tendency on the part of analysts to avail themselves of biological methods, and the application of pure cultures of yeasts and other lowly organisms has rendered it possible successfully to attack analytical problems which had previously been regarded as incapable of solution. The method is clearly one which must be applied with very great caution, and demands a certain amount of biological training on the part of the operator. Among others, Lindner has done a great deal of work in this direction, and attention may be called to an interesting paper by König and Hörmann,[78] in which some very useful confirmatory work is recorded, and which contains the results of experiments made for the purpose of ascertaining to what extent the dextrins obtained by the limited action on starch of acids and of diastase respectively may be separated from the sugars. It is pointed out *inter alia* that the dextrinous body present in honey is of an entirely different character from the dextrins prepared as above mentioned. This paper will well repay careful perusal by all who are actively interested in carbohydrate analysis. It is interesting to note that two species of torulæ are capable of effecting a separation of dextrose and fructose from sucrose, and it seems very probable that a further study of the torulæ (as opposed to the true yeasts) might be productive of useful results. Neuberg[79] has shown that, by the action of emulsin, raffinose is hydrolysed into a mixture of saccharose and *d*-galactose, and, in conjunction with Marx,[80] has suggested the use of emulsin as a test for the presence of raffinose in raw cane sugars. In view of the fact that the melting points of the osazones are frequently made use of for purposes of identification, a paper by Tutin[81] is of considerable importance. The author shows that when *d*-phenylglucosazone is purified by recrystallisation from a mixture of pyridine and alcohol, the compound melts at 217°. The melting point of 205°, which was originally given by E. Fischer and the correctness of which has always been assumed, must therefore apparently be abandoned. It may be recalled that the melting point of α-acrosazone has already been found to be 217°, instead of 205° as originally stated, and it will be interesting to ascertain whether similar differences will be observed in the case of the osazones of other sugars. The nature of the influence exerted by basic lead acetate on the rotation of sucrose in aqueous solution has been investigated by Bates and Blake,[82] who show that von Lippmann's statement that basic acetate is without effect is incorrect. The authors find that on the progressive addition of the acetate there is first a lowering of the rotation, and then a gradual rise, which they ascribe to the formation of soluble lead sucrates having rotations differing from that of sucrose itself. Lintner[83] describes a polarimetric method for the estimation of starch in cereals, which has been further examined by Canet and Durieux,[84] who have recorded a number of results with cereals and other starch-containing products. The method certainly appears to be capable of giving good results, and will doubtless be useful as a substitute for the more lengthy and laborious diastase conversion method when rapid results are required.

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[78] *Abstr.*, 1907, ii, 202.

[79] *Ibid.*, i, 388.

[80] *Ibid.* ii, 408.

[81] *Proc.*, 1907, **23**, 250.

The analysis of indigo has, during recent years, been made the subject of a considerable amount of experimental work, and has furnished a good deal of controversy.

The attention of all chemists who are interested in this matter is directed to an important communication by Orchardson, Wood, and W. P. Bloxam,[85] constituting the second part of their paper on "The Analysis of Indigo." This contains an account of experiments made for the purpose of isolating the impurities present in cake indigo, and of ascertaining how these substances behave with the analytical reagents employed, and to what extent they interfere. A new method is described for the estimation of indigotin obtainable from the leaf, and the authors appear to be confirmed in their opinion that the separation of the indigotin in the form of a purified compound (potassium indigotintetrasulphonate) must constitute the first step in the analytical process. The method of Bergtheil and Briggs, which was referred to in my previous Report,[86] is adversely criticised by the authors, who state that it gives irregular results. The attention of those interested in this matter may be also directed to two other communications, one by Bergtheil and Briggs,[87] and the other by Gaunt, Thomas, and Bloxam,[88] both dealing with the estimation of indigotin in the plant. The writer of this Report, in common with several other chemists, has had an opportunity of witnessing a demonstration of the tetrasulphonate process, and in his opinion there can be no doubt that the indigotin is quantitatively separated from the impurities with which it is associated in the crude product, and that, to say the least of it, the process marks a great advance.

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[82] *Abstr.*, 1907, ii, 406.
[83] *Ibid.*, 823.
[84] *Bull. Soc. Chim. Belg.*, 1907, **21**, 329.
[85] *Abstr.*, 1907, ii, 203.
[86] *Ann. Report*, 1906, 215.
[87] *Abstr.*, 1907, ii, 415.
[88] *Ibid.*, 1908, ii, 76.

The estimation of choline and other bases in vegetable and other extracts is a matter of considerable importance to the physiological chemist, and any improvement in the methods for separating and estimating these substances is welcomed by a large and increasing body of workers. Staněk's periodide method for the separation of choline and betaine, to which reference was made in the last Report,[89] appeared to constitute a very useful addition to existing methods, but Kiesel[90] has shown that it cannot be applied to the estimation of choline in such materials as plant extracts, since these contain many other bases which seriously interfere with the accuracy of the results.

During the past few years, rubber experts have shown a growing tendency to attach importance to the results of chemical analysis when forming an opinion as to the value of commercial rubbers. At the present time, the most important constituent, caoutchouc, is almost invariably estimated by difference, and the desirability of obtaining a direct method for its estimation is obvious. Several such methods have been suggested, but by far the most promising are those in which the rubber is submitted to the action of nitrous fumes, and the resulting so-called "nitrosate" weighed. In a previous Report,[91] it was mentioned that Harries and Alexander had found that the nitrogen compound originally obtained by Weber was not at all definite. In a recent communication, Alexander[92] has recorded the results of further work in this direction, and has suggested a method which, if carefully carried out, would appear to be capable of giving fair results. Much work remains to be done before it can be said that a satisfactory process for the direct estimation of caoutchouc has been devised, but Alexander's method appears to offer a solid foundation for further building, and his results, moreover, may throw a good deal of light on the constitution of caoutchouc and on the nature of vulcanisation.

Another promising direct method is that of Budde, which is based on the readiness with which caoutchouc unites with bromine to form an insoluble tetrabromide. A carbon tetrachloride solution, containing both bromine and iodine, is added to a solution of the rubber, also in carbon tetrachloride, and the tetrabromide, which is precipitated by the addition of alcohol, is collected, washed, dried, and weighed. Budde has shown that the compounds formed by the action of bromine on certain unsaturated rubber resins are soluble in the above mixture of carbon tetrachloride and alcohol, and, consequently, do not interfere with the results. Two papers, the one by Budde,[93] and the other by Axelrod,[94] have recently been published, from which it would appear that this method, with slight modifications, is applicable to the direct determination of caoutchouc in certain vulcanised rubbers. The further development of these two direct methods will be watched with very considerable interest by all who are concerned in the analysis and commercial evaluation of rubber.

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[89] *Ann. Report*, 1906, 220.

[90] *Abstr.*, 1907, ii, 994.

[91] *Ann. Report*, 1905, 200.

[92] *Abstr.*, 1907, i, 433.

Analysis of Foods and Drugs.

Comparatively little progress has been made during the year in connexion with the analysis of milk and milk products. Analysts are well aware that the accurate estimation of fat in certain milk preparations is not always an easy matter, and that different methods are required in dealing with various materials. Hals and Klykken[95] have recorded the results they have obtained in the estimation of fat in sweetened and unsweetened condensed milks by a number of standard processes, and are of opinion that the Gottlieb and the Gerber methods are the most accurate for the purpose. Cochran[96] has investigated the behaviour of Wiley's acid mercuric nitrate solution, and has shown that it has no effect on the polarisation of lactose, and that at temperatures below 15° its inverting action on sucrose is very slight indeed. In these circumstances, it can be used with good results for the estimation of lactose and sucrose in sweetened condensed milk. Although a good deal of attention has been devoted during the year to the important question of the detection and estimation of cocoanut oil in butter, the subject has not been very much advanced, and there can be little doubt that the Polenske method (either as originally published or modified) and the phytosterol acetate test combined are still capable of furnishing the most trustworthy indications. Reference should, however, be made to a communication by Hinks,[97] who has proposed a direct qualitative test for the presence of the cocoanut oil. This is a micro-crystallographic method, and in the hands of its author has given distinct indications when the cocoanut oil was present only to the extent of 5 per cent. This method appears to be useful, and the advantage of possessing a characteristic test for this troublesome adulterant will be apparent. Most analysts know how greatly the distillation conditions may affect the Reichert-Meissl, and especially the Polenske, values of fats, and Goske[98] has devoted some attention to the influence of the mode of heating on the Polenske number. This paper may be read with advantage, if only to emphasise the importance of adhering strictly to a standard set of conditions. In view of the importance to analysts of the phytosterol acetate test, a paper on this subject by Jaeger[99] is deserving of attention. Windaus and Hauth[1] showed that Calabar beans contained two isomeric phytosterols having very different melting points, and it is probable that other isomerides exist. Jaeger[2] shows that the melting point curves for mixtures of cholesteryl acetate, with the acetates of the two above-mentioned isomerides, afford evidence that the melting points of such mixtures are not at all trustworthy criteria of composition, and it is clear that the indications of the test must be interpreted with considerable caution. While dealing with this subject, attention may be drawn to a paper by Lewkowitsch[3] on the determination of paraffin in the unsaponifiable matter from animal fats. The author confirms the accuracy of Polenske's method,[4] and shows that good results can be obtained by determining the saponification value of the mixture of the acetates and the paraffin. The esterification of fats and oils by the method of Haller, to which the objectionable name "alcoholysis" has been given, has been applied with slight modification by Hanuš[5] to the detection of cocoanut oil in butter, and the recorded results indicate that the method may at least serve as a useful auxiliary one. Further work on the "silver" process of Wijsman and Reijst has confirmed the view that the results are untrustworthy, and that the values do not afford any certain criterion of the purity of butter fat. It should be noted that Siegfeld[6] and others have shown that the feeding of cattle with cocoanut cake and beetroot leaves may appreciably affect the Polenske and iodine values of the butter. Several chemists, including Kreis and Canzoneri, have endeavoured to isolate the constituent of sesame oil which produces the red coloration with furfuraldehyde and hydrochloric acid, but without complete success. Malagnini and Armanni[7] appear to have been more fortunate, inasmuch as they have separated a crystalline substance, melting at 57°, having the formula $C_7H_6O_3$, which gives, with the above-mentioned reagents, a very intense coloration. The authors regard this substance as a methylene ester of hydroxyquinol, and point out that it does not exist as such in the oil, but is formed from a more complex compound (which they have also isolated) by the action of dilute mineral acid. This reaction for sesame oil is a very important one, especially in view of the fact that in several countries sesame oil is compulsorily added to margarine for the purpose of earmarking that substance and of facilitating its recognition in butter. The literature of this test is voluminous, and much has been written as to the conditions which affect the sensitiveness of the reaction. Although samples of sesame oil which do not yield the red coloration are undoubtedly very rare,[8] it cannot be overlooked that several observers, including Weigmann and Soltsien, have recorded cases in which the reaction could not be obtained, and it is also well known that samples of sesame oil differ very widely in the intensity of the coloration which they produce. Lauffs and Huismann[9] have been working on this subject, and have recorded another instance of a rancid sample which failed to respond to the test. These authors appear to be of opinion that this is due to the formation of a condensation product of the sesamol with the aldehydic substance present in the rancid oil, and they recommend the addition of a proportion of cottonseed oil to the fat to be tested, which is said to prevent the interfering effect of rancidity and to render the test more sensitive. However this may be, it is clear that this question requires further study, for in view of these recorded observations chemists are not justified in considering a negative result when applying the Baudouin test as a conclusive proof of the absence of sesame oil.

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[93] *Gummi. Zeit.*, 1907, **21**, 1205.

[94] *Ibid.*, 1229.

[95] *Zeitsch. Nahr. Genussm.*, 1907, **13**, 338.

[96] *Abstr.*, 1907, ii, 586.

[97] *Analyst*, 1907, **32**, 160.

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[98] *Zeitsch. Nahr. Genussm.*, 1907, **13**, 491.

[99] *Abstr.*, 1907, ii, 315.

[1] *Ibid.*, i, 129.

[2] *Ibid.*

[3] *Chem. Rev. Fett. Harz. Ind.*, 1907, **14**, 51.

[4] *Abstr.*, 1905, ii, 870.

[5] *Zeitsch. Nahr. Genussm.*, 1907, **13**, 18.

[6] *Ibid.*, 513.

[7] *Chem. Zeit.*, 1907, **31**, 884.

The estimation of tartaric acid in the presence of malic and succinic acids is a frequently recurring problem in the analysis of foodstuffs and other products, and chemists will no doubt critically examine a method recommended by von Ferentzy.[10] This is based on the insolubility of basic magnesium tartrate in aqueous alcohol of 50 per cent. strength, and the ready solubility in that solvent of the corresponding salts of malic and succinic acids. Two other papers dealing with the same subject which are worthy of attention are by Jörgensen[11] and by Kunz and Adam.[12] Some interesting work has been recorded during the year by T. B. Wood[13] in connexion with the important question of the "strength" of wheat flour. Perhaps the most noteworthy observations are those from which it is sought to show that the strength of flour is largely conditioned by the ratio of protein to mineral matter, small quantities of certain salts having, as is well known, an appreciable effect on the physical properties of the proteins. The extension of this work will be watched with interest. The estimation of creatine and creatinine in meat and other extracts has attracted the attention of several chemists during the past year. Baur and Barschall[14] appear to have been the first to apply the colorimetric method of Jaffé (based on the red coloration produced when picric acid is added to an alkaline solution containing creatinine) to the examination of meat extracts, and their results were subsequently extended by Grindley and Woods.[15] Hehner[16] has shown that in applying this method it is necessary to ensure the presence of an excess of picric acid, and to match the coloration in as strong solutions as possible in order to avoid the errors produced by the dissociation of the coloured compound. The method affords a valuable means of distinguishing between extracts of meat and extracts made from yeast, since the latter are practically devoid of either creatine or creatinine. It is perhaps worthy of note that extract of crab is also, according to Ackermann and Kutscher,[17] free from those bases. Winton and Bailey[18] point out that meat which has undergone even slight decomposition yields volatile sulphur compounds when distilled with phosphoric acid, as in the ordinary estimation of sulphites. These are oxidised by bromine water, and so lead to an over-estimation of any sulphurous acid present. A method for obviating this difficulty is proposed, and the matter is deserving of the attention of food chemists, as it may apply to other substances than meat, and is especially of importance in countries like the United States of America, where the presence of sulphites in food-stuffs is regarded so seriously. Woodman and Talbot[19] call attention to the presence of fluorine as a very general constituent of malt, and consequently of malt liquors, and suggests one part in one hundred thousand as a maximum limit for fluorine normally present. For distinguishing between natural and artificial colouring matters in wines, Jean and Frabot[20] recommend warming with formaldehyde and hydrochloric acid, and the subsequent addition of ammonia. A colourless filtrate is said to be obtained with all natural wines. Of a number of papers which have been published dealing with the analysis of potable spirits, reference need only be made to one by Bedford and Jenks[21] on the estimation of the higher alcohols. These authors are probably correct in stating that, whilst the results obtained by the Allen-Marquardt process are good in the case of amyl alcohol, the intermediate alcohols, such as butyl and propyl, largely escape determination, and it is obvious that *iso*propyl alcohol cannot be estimated at all. The method they propose resembles that of Beckmann, in that the alcohols are extracted by carbon tetrachloride, and then converted into nitrous esters. Instead, however, of estimating these by oxidation with permanganate, the authors treat them with potassium iodide, and determine the liberated iodine. This communication is worthy of attention, but the authors' claim to distinguish between amyl alcohol, on the one hand, and propyl and butyl, on the other, will scarcely be admitted by analysts generally.

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[8] Lewkowitsch, in a private communication to the writer of this Report, states that he has never yet met with a sample which failed in this respect, although he has examined many which were old and undoubtedly rancid.

[9] *Chem. Zeit.*, 1907, **31**, 1023.

[10] *Abstr.*, 1907, ii, 991.

[11] *Ibid.*, 312.

[12] *Zeitsch. anal. Chem.*, 1907, **46**, 261.

[13] *Abstr.*, 1907, ii, 810, and *J. Agric. Sci.*, 1907, **2**, 139.

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[14] *Arb. Kaisl. Gesundheitsamt*, **24**, 562.

[15] *Abstr.*, 1907, ii, 187.

[16] *Pharm. J.*, 1907, **78**, 683.

[17] *Abstr.*, 1907, ii, 283.

[18] *J. Amer. Chem. Soc.*, 1907, **29**, 1499.

[19] *Ibid.*, 1362.

[20] *Abstr.*, 1907, ii, 320.

[21] *Ibid.*, 405.

Many papers have been published during the year describing new alkaloidal reactions (usually colour reactions), but these are scarcely of sufficient importance to merit special reference. An exception may, perhaps, be made in favour of two papers by Reichard,[22] who describes somes new reactions of scopolamine and yohimbine. Knorr[23] appears to have been the first to suggest the use of picrolonic acid (4-nitro-1-*p*-nitrophenyl-3-methyl-5-pyrazolone) as a precipitant for alkaloids; Warren and Weiss[24] have experimented with this substance, and find that it is a more delicate test than picric acid for coniine, strychnine, and morphine, and Matthes and Rammstedt[25] have applied this reagent to the assay of nux vomica, hydrastis, and jaborandi, and their galenical preparations. The results appear, as a rule, to be good, and the method is likely to be useful. The same authors[26] have also obtained good results when using this reagent in the estimation of narcotine, codeine, and morphine. Tschirch and Edner[27] have investigated the constituents of English and French rhubarb, and have shown that a diazotised *p*-nitroaniline solution constitutes a useful reagent for the evaluation of that drug. The results when working with pure emodin were accurate, and the method appears to mark a distinct advance on the colorimetric process. It may be pointed out that the found percentages of hydroxymethylanthraquinones (expressed for convenience in terms of chrysophanol) range from 4·24 per cent. in the case of the Shanghai to 1·58 per cent. in the case of the French product.

Bougault[28] has shown that the reagent (a solution of hypophosphorous acid in hydrochloric acid) which he previously recommended for the detection of cacodylic and methylarsonic acids is applicable to the detection and estimation of arrhenal (disodium methylarsonate) and atoxyl (sodium anilinoarsonate). The author finds that the black substance which is produced when the above-mentioned reagent is allowed to act on arrhenal has the formula $(\mathbf{MeAs})_x$, and that it is quantitatively oxidised by nitric acid or by iodine to methylarsonic acid in accordance with the equation: $MeAs + 4I + 3H_2O = MeAsO(OH)_2 + 4HI$. The atoxyl compound is similarly oxidised, and may be estimated in the same way. The same author[29] finds that methylarsine di-iodide and oxide may be estimated by titrating their aqueous solutions with a solution of iodine in potassium iodide.

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[22] *Abstr.*, 1907, ii, 915.
[23] *Ibid.*, 1897, i, 314.
[24] *Ibid.*, 1907, i, 869.
[25] *Ibid.*, ii, 592.
[26] *Ibid.*, 1908, ii, 75.
[27] *Ibid.*, 1907, ii, 501, 515.
[28] *Ibid.*, 828.

Toxicological Analysis.

Calvi and Malacarne[30] show that alcohol materially retards the decomposition of cyanides, so that hydrocyanic acid may be detected in organs which have been preserved in alcohol, even at the end of some considerable time. Schaefer[31] has investigated the natural occurrence of arsenic in the human body, and has detected very appreciable traces in the hair, skin, liver, kidneys, brain, and thyroid glands, and has thus confirmed the conclusion arrived at by other workers that arsenic in traces must be considered a "normal" constituent of the human organism. He expresses the opinion that the arsenic is localised largely in the nucleins, a suggestion which seems to find some support in the marked readiness with which the yeast cell takes up small amounts of arsenic. These results, supporting as they do those already arrived at by W. Thomson and others, appear to indicate that no special significance can be attached to the discovery of traces of arsenic in many of the organs of the body. Bolland and Franzos,[32] in an investigation of two cases of phosphorus poisoning, where the bodies had been buried for four months, found that it was impossible to obtain any definite indications of the presence of phosphorus by either the Mitscherlich or the Dusart-Blondlot method. During recent years, the guaiacum test for oxyhæmoglobin has been studied by a number of investigators, especially with reference to the production of the coloration by other substances than blood. Bolland[33] finds that the presence of traces of iron in the solvents which are ordinarily employed in the treatment of blood stains gives rise to the well-known blue colour, but that this is inhibited by citric acid. In the presence, however, of oxyhæmoglobin, the blue coloration is obtained, citric acid notwithstanding. Buckmaster,[34] dealing with the same subject, points out that the reaction is due to the iron of the hæmoglobin, iron-free derivatives of that substance, such as hæmatoporphyrin, failing to give it. In confirmation of this, Lesser [35] finds that the blood of invertebrates, which contains no hæmoglobin, does not give the reaction. The benzidine test for blood proposed by Schlesinger and Holst has been investigated by Utz,[36] who finds that it is more delicate than the guaiacum reaction, provided that the reagents are freshly prepared. Van Rijn,[37] in the course of a study of the distribution of morphine in the animal organism, administered 200 milligrams of the hydrochloride to an animal, which was killed six hours later. By the ordinary process of extraction, about 84 per cent. of the total amount administered was recovered, and the author shows that the alkaloid tended to accumulate very largely in the urine.

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[29] *Abstr.*, 1907, ii, 916.
[30] *Ibid.*, 409.
[31] *Ibid.*, 371.
[32] *Chem. Zeit.*, 1907, **31**, 8.
[33] *Abstr.*, 1907, ii, 660.
[34] *Ibid.*, 660.

Apparatus.

The following list contains reference only to those new pieces of apparatus which have been described in recognised journals, and which appear to be of real utility. The titles are not always exactly those given by the authors, but have been, in some cases, more or less altered in order to indicate more clearly the nature of the apparatus in question.

In connexion with apparatus, it may be mentioned that Heraeus [38] has shown by direct experiment that hydrogen from the flame of a Bunsen burner diffuses through platinum, and may bring about the reduction of ferric oxide and other reducible substances. These experiments throw a good deal of light on the corrosion and ultimate destruction of platinum crucibles.

"The Kennicott-Sargent Colorimeter" (*Chem. Engineer*, 1907, **5**, 213).

"A portable milk colorimeter." A. Bernstein (*Chem. Zeit.*, 1907, **31**, 727).

"New melting point thermometer." G. Müller (*Chem. Zeit.*, 1907, **31**, 571).

"New apparatus for determining melting points." J. Thiele (*Abstr.*, 1907, ii, 330).

"A calorimeter for volatile liquid fuels." W. H. Rawles (*J. Soc. Chem. Ind.*, 1907, **26**, 665).

"A new portable gas generator." A. W. Browne and M. J. Brown (*Abstr.*, 1907, ii, 678).

"A constant pressure gas generator." A. W. Browne and M. J. Brown (*Abstr.*, 1907, ii, 679).

"New gas-generating apparatus." E. Steiger (*Abstr.*, 1907, ii, 339).

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[35] *Abstr.*, 1907, ii, 827.
[36] *Ibid.*, 916.
[37] *Ibid.*, 995.
[38] *Ibid.*, 969.

"New gas-generating apparatus." A. Burger and M. W. Neufeld (*Abstr.*, 1907, ii, 339).

"New apparatus for gas analysis." O. Pfeiffer (*Abstr.*, 1907, ii, 194).

"A gas-developing apparatus." A. Kleine (*Abstr.*, 1907, ii, 446).

"An improved gas generator." F. Southerden (*Chem. News*, 1907, **95**, 207).

"Apparatus for crystallising and filtering in indifferent gases." W. Steinkopf (*Abstr.*, 1907, ii, 161).

"A new absorption and washing apparatus for gases." B. Phyl (*Zeitsch. anal. Chem.*, 1907, **46**, 150).

"New absorption vessels for elementary analysis." O. Carrasco (*Chem. Zeit.*, 1907, **31**, 342).

"New form of potash bulb." P. Malherbe (*Ann. Chim. anal.*, 1907, **12**, 318).

"Drying apparatus for elementary analysis." O. Mittelbach (*Chem. Zeit.*, 1907, **31**, 551).

"Simple apparatus, with stirrer, for treating a liquid at its boiling point with two or more gases." N. L. Gebhard (*Proc.*, 1907, **23**, 34).

"Boiling and distillation of foaming liquids." R. Fanto (*Zeitsch. angew. Chem.*, 1907, **20**, 1233).

"Two fractionating columns for readily volatile liquids." H. Schlemmer (*Chem. Zeit.*, 1907, **31**, 692).

"Apparatus for distillation and desiccation at low temperatures." D'Arsonval and Bordas (*Ann. Chim. anal.*, 1907, **12**, 4).

"Modifications of Dennstedt's method of combustion analysis." R. Baumert (*Abstr.*, 1907, ii, 909).

"Platinum resistance furnace for melting points and combustions." S. A. Tucker (*Abstr.*, 1907, ii, 842).

"A simple fat extraction apparatus." G. S. Fraps (*Abstr.*, 1907, ii, 314).

"New extractor for the determination of fat by means of carbon tetrachloride." F. Vollrath (*Abstr.*, 1907, ii, 514).

"An improved fat extraction apparatus." J. van Leeuwen (*Chem. Zeit.*, 1907, **31**, 350).

"Extractor for use with small quantities of material." C. L. Jackson and J. E. Zanetti (*Abstr.*, 1907, ii, 859).

"A new eudiometer for use in the analysis of mixtures of air and inflammable gases." J. Meunier (*Abstr.*, 1907, ii, 989).

"Some new ureometers." M. E. Pozzi-Escot (*Abstr.*, 1907, ii, 414; compare Albert Garcia, *Abstr.*, 1907, ii, 994).

"Modification of Regnard's ureometer." M. E. Pozzi-Escot (*Abstr.*, 1907, ii, 724).

"Standardisation of Engler's Viscosimeter" (*Zeitsch. angew. Chem.*, 1907, **20**, 832).

"A modified Engler viscosimeter." L. Ubbelohde (*Chem. Zeit.*, 1907, **31**, 38).

"A new filter paper of cotton cellulose" (*Chem. Zeit.*, 1907, **31**, 465).

"A simple arrangement for the filtration of alkaline liquids (in air free from carbon dioxide). R. Rinne (*Abstr.*, 1907, ii, 447).

"Pressure filter for laboratory use" (*Chem. Trade J.*, 1907, **41**, 305).

"A new sublimation apparatus." V. Schworzoff (*Abstr.*, 1907, ii, 160).

"A self-filling burette." N. J. Lane (*Abstr.*, 1907, ii, 390).

"Burette reading." P. Kusnetzoff (*Abstr.*, 1907, ii, 809).

"Arrangement for reading thermometers, burettes, &c." L. H. Zeller (*Chem. Zeit.*, 1907, **31**, 115).

"Water-jet blower of very simple construction." S. M. Revington and I. G. Rankin (*Abstr.*, 1908, ii, 30).

"A convenient air-bath and hot-plate." E. D. Campbell (*Abstr.*, 1907, ii, 446).

"Asbestos wire gauze." H. Carliczek (*Chem. Zeit.*, 1907, **31**, 500).

"Simple lamp for monochromatic light." E. Beckmann (*Abstr.*, 1907, ii, 209).

"A new centrifugal apparatus for laboratory use." T. Körner (*Abstr.*, 1907, ii, 161).

"Improved Liebig's condenser." H. R. Ellis (*Abstr.*, 1907, ii, 160).

"Some new forms of apparatus." W. M. Dehn (*Abstr.*, 1907, ii, 755).

"Portable photometer." J. A. Evans (*J. Amer. Chem. Soc.*, 1907, **29**, 1009).

"A mercury joint in place of cork or rubber in organic analysis." J. Marek (*Abstr.*, 1907, ii, 909).

"Device for filling bottles from carboys." R. M. Hughes and C. Barrow (*J. Amer. Chem. Soc.*, 1907, **29**, 241).

"The use of nickel crucibles in quantitative analysis, and the composition of the so-called "Nickel Soot." R. Kržižan (*Abstr.*, 1907, ii, 390).

"Apparatus for absorbing acid vapours given off during the assay of gold, silver, &c." Dard (*Abstr.*, 1908, ii, 72).

"Apparatus for obtaining standard temperatures in drying ovens." J. Habermann (*Abstr.*, 1908, ii, 17).

"Collodion membranes for dialysis." S. L. Bigelow and A. Gemberling (*Abstr.*, 1907, ii, 933).

"Simple apparatus for analytical purposes." J. McC. Sanders (*Proc.*, 1907, **23**, 232).

"New mercury-drop tensimeters." W. M. Dehn (*J. Amer. Chem. Soc.*, 1907, **29**, 1052).

"Method of obtaining the flame spectrum of metals." G. A. Hemsalech and C. de Watteville (*Chem. Zeit.*, 1907, **31**, 693).

"An automatic vacuum regulator." A. E. Andrews (*Chem. News*, 1907, **96**, 76).

"A simple means for the recognition of the colour of small quantities of faintly-coloured liquids, and its use in microchemical analysis." F. Emich and J. Donau (*Abstr.*, 1907, ii, 809).

"Apparatus for the estimation of carbon dioxide in carbonates." P. Malherbe (*Abstr.*, 1907, ii, 719).

"Apparatus for the supply of carbon dioxide in the determination of nitrogen in organic compounds by the absolute method." G. Young and B. Caudwell (*Abstr.*, 1907, ii, 394).

"Apparatus for use in testing substances for phosphorus." J. Habermann (*Abstr.*, 1908, ii, 17).

"Apparatus for the continuous preparation of pure oxygen for use in organic analysis." A. Seyewetz and L. Poizat (*Abstr.*, 1907, ii, 162).

"Improved form of apparatus for the rapid estimation of sulphates and salts of barium." W. R. Lang and T. B. Allen (*Proc.*, 1907, **23, 187**).

"Apparatus for the estimation of sulphur (in iron)." Von Nostitz and Jänkendorf (*Abstr.*, 1907, ii, 393).

"New laboratory method for the preparation of hydrogen sulphide." F. R. L. Wilson (*Proc.*, 1907, **22**, 312).

"Apparatus for the gasometric determination of hydrogen peroxide." W. M. Dehn (*Abstr.*, 1907, ii, 906).

"Apparatus for determining the coefficients of expansion of oils which solidify at low temperatures (crude petroleum)." J. Gruszkiewicz and W. Bartoszewicz (*Petroleum*, 1907, **2**, 525).

"Electrolytic oxidation in quantitative analysis." O. Gasparini (*Abstr.*, 1907, ii, 650).

"Apparatus for the comparative observation of fluorescence." H. Ley and H. Gorke (*Abstr.*, 1907, ii, 920).

"A Filter-tube." P. W. Shimer (*Chem. Engineer*, 1907, **6**, 197).

"Laboratory apparatus for the evaporation of liquids by radiation from above." H. J. S. Sand (*J. Soc. Chem. Ind.*, 1907, **26**, 1225).

"A gas-generating apparatus." Eugen Müller (*Abstr.*, 1908, ii, 129).

As year by year the number of published papers dealing with analytical subjects increases, the responsibility and difficulty attaching to the task of presenting this report become greater. It is clear that exigencies of space render it impossible to refer to a very large number of communications, many of which record quite useful observations, and the author is compelled to select for notice the comparatively few which, in his judgment, are of special importance in relation either to theory or laboratory practice.

ALFRED CHASTON CHAPMAN.

PHYSIOLOGICAL CHEMISTRY.

In the report which I wrote last year I began by regretting that it was not my good fortune to be able to chronicle any great discovery. The same is also true this year. Last summer the physiologists met at Heidelberg for their triennial International Congress, but there was nothing forthcoming of epoch-making importance. Indeed, most of the numerous papers read dealt with matters which were already familiar, for with few exceptions the authors appeared to think it necessary to present a *réchauffé* of all that they had been doing within the preceding three years. This, however, was by no means uninteresting, for any matter seems more real when presented by word of mouth, especially when it is illustrated by actual experiments. Many of the great problems at present on hand will need many years' work yet before it is possible to draw general conclusions; and this is illustrated by the steady progress which Emil Fischer, Abderhalden, and their colleagues are making in their attempts to unravel the mysteries of the protein molecule. One characteristic of modern physiological research was strikingly brought out at the recent Congress, and that is the ever-increasing part which chemistry is playing in aiding the solution of biological problems. Two of the four sections into which the Congress divided itself dealt with questions of bio-chemistry, and even then some of the chemical papers overflowed into other sections. It is, however, not necessary to labour this point, for the Faraday lecture, which Professor Emil Fischer so recently delivered before the Chemical Society, has brought it out more forcibly and eloquently than anything I am able to write.

The year's work has been far from barren; a glance through the abstracts in our Journal will show it has, in fact, been more voluminous than ever. This is a matter for congratulation, for each paper is a brick of varying dimensions in the great edifice of knowledge which is gradually being reared. But to an annual reviewer the plethora of work increases his difficulties in selecting subjects for comment within the limits of space imposed upon him by the Editor. The proteins, as usual, must come first; then it will be necessary to take up the subject of digestion, accurate knowledge of which is progressing by leaps and bounds owing to the new methods employed by E. S. London and his co-workers on the lines initiated by his great fellow-countryman Pawloff. Then there are some important questions of general metabolism which have risen to the fore, including some relating to the gaseous interchanges in the tissues, and the exchange of material in the fœtus. Enzymes, of course, are always with us, and among these rennet has been attracting considerable attention of late.[1] The great question of immunity has now a literature of its own, and a terminology of its own, which increases the difficulties of those not actually *au courant* with the subject. This I do not propose to touch, except incidentally, in my present article. I propose, however, to depart this year from my usual custom and deal somewhat fully with a matter which has been monopolising the attention of the workers in my own laboratory, and I do so not from any egotistical motives, but simply because it will furnish me with the necessary peg on which to hang related questions which have been taken up elsewhere. The subject I refer to is one of some intrinsic interest, namely, the chemistry of nervous tissues; it is, of course, a long way from the phosphatides and other constituents of the brain as studied in the test-tube to an understanding of the phenomena of cerebral function; nevertheless, one can foresee a time when even the psychologist will not be fully equipped for his labours without the assistance of his chemical brethren. On the pathological side I propose to deal with one subject only, namely, that of diabetes, the papers on which have of late been unusually numerous. Whether they have made the subject any plainer is a matter for doubt; at any rate they have shown that some of our previous views are in part incorrect or need reconsideration, and thus the way is opened to renewed investigation on a surer basis.

Proteins.

Protamines and Histones.—Kossel has for some time past regarded the protamines as the simplest members of the protein family, and obviously to understand the more complex substances in the group it is first necessary to attack the constitution of the simplest. One welcomes, therefore, Kossel's most recent pronouncement on the subject. There are degrees of complexity among the protamines themselves, and the simplest are those of the salmine group (salmine, clupeine, scombrine). Kossel and Pringle[2] have shown that in these 8/9ths of the nitrogen present is in the form of arginine, and the remaining 1/9th as monoamino-acids (alanine, serine, aminovaleric acid, and proline), two or more of which may be present. As arginine contains four atoms of nitrogen, it follows that one molecule of monoamino-acid is present to every two molecules of arginine, and such protamines are therefore diarginyl compounds. Reasons are given for believing that the linking is symmetrical, thus: aab', aab'', aab''' where a is arginyl and b', b'', b''' monoamino-groups. The protones which are obtained on digestion as the first cleavage products of the protamines also contain 8/9ths of their nitrogen in the form of arginine. Diarginylalanine will have a molecular weight 401, diarginylserine 417, diarginylproline 427, and diarginylaminovaleric acid 429. The molecular weight of the protones by the boiling-point and freezing-point methods of investigation was found to be from 419 to 423. It therefore appears that they are mixtures of the diarginyl compounds just enumerated. By the action of nitrous acid on this mixture ornithine is split off, from which it is argued that the symmetric arrangement is probably baa rather than aab or aba.

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[1] The principal points under discussion have been whether the change of caseinogen into casein is physical or chemical; and whether or not pepsin and rennet are identical; the view that they are the same originally advanced by Pawloff is gaining ground; a good summary of the controversy is given by Gewin (*Zeitsch. physiol. Chem.*, 1907, **54**, 32).

In histones, diamino-acids are again the most important cleavage products, arginine accounting for 25 per cent. of the nitrogen and lysine for 7 to 8 per cent. The first product of gastric digestion is termed histopeptone; this yields the same proportion of arginine, and it appears to be a chemical unit, not a mixture as the protones are. Moreover, histopeptone was obtained from several animal tissues and organs, most from the spleen and least from the liver. Attempts to obtain it from various vegetable proteins failed (T. Krasnosselsky[3]).

Spider's Silk.—The recent work of Emil Fischer[4] on the silkfibroin produced by the Madagascar spider shows that this substance is also of a comparatively simple nature, and that it bids fair to oust the protamines from their position at the bottom of the list. Like the fibroin from ordinary silk, it yields as its cleavage products mainly monoamino-acids, diamino-acids accounting for only 5·2 per cent. Further, the various products differ but little in kind and quantity from those obtained from the silkworm product. This investigation awakens many interesting reflections; it shows us in the first place how secreting organs of such great morphological difference as the spinning pap of a spider and the glands of a silkworm can form products so similar chemically. The one is a carnivorous animal, the other lives on comparatively cheap vegetable matter, and yet the adaptability of the laboratory of the living cell is so far-reaching as to lead to the formation of an almost identical secretion in the two cases. It seems almost hopeless at present to expect that even Professor Fischer can go and do likewise, and yet so thorough is the knowledge of the cleavage products obtained by accurate analysis that he has stated he has selected silk-fibroin as the protein in particular in which to attempt a synthesis.

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[2] *Abstr.*, 1907, i, 266. [3] *Ibid.*, 267. [4] *Ibid.*, ii, 566.

Reversible Protein-hydrolysis.—While we await the outcome of this great endeavour, it is interesting to note that from the other side of the Atlantic comes the first successful attempt to synthesise a protein by means of ferment action. The amino-acids resulting from the hydrolysis of a protamine were placed by A. E. Taylor[5] in concentrated solution in contact with trypsin. The trypsin employed was a very resistant one prepared from a mollusc. At the end of five months 1·6 grams of protamine were obtained, 400 grams of protamine sulphate having been originally employed for the hydrolysis. A blank experiment in which the trypsin had been boiled gave negative results. The term synthesis through ferment action is, as the author points out, in the direct sense a misnomer; the ferment, of course, simply accelerates the reaction of synthesis, but as the result shows, even in the presence of the ferment, the velocity is slow; still, if the result is sure, and there is no necessity to doubt that, the experiment is in every sense a noteworthy one. A somewhat similar result with pepsin and paranuclein was obtained in the same laboratory by T. B. Robertson,[6] and more recently by E. Zak[7] in connexion with the proteolytic ferment of *Bacillus pyocyaneus*.

The Cleavage of Proteins and Polypeptides.—In the body protein is successively acted on by gastric juice, pancreatic juice, and erepsin, and so it is broken down in stages to its simplest cleavage products. The importance of gastric digestion is far from clear, except in the case of a few proteins which are not readily attacked by pancreatic juice. It is well known that extirpation of the stomach, if the continuity of the alimentary canal is secured by appropriate surgical methods, is not a fatal operation either in animals or men, and the view has found expression in some physiological writings that the stomach is therefore a useless organ; the vermiform appendix, the source of many troubles, has been placed in the same category. This extreme view, at any rate in relation to the stomach, is not really justifiable. That an animal can get on pretty well without a stomach is testimony to the wonderful power of compensation the body possesses, and is no proof of the uselessness of the organ which has been removed. It was with the view of clearing up the doubt as to the exact rôle gastric digestion plays that Abderhalden and Gigon[8] undertook a research in which edestin (the globulin of hemp seed) was subjected *in vitro* to the successive action of the juices enumerated. So far as the main object of the experiments was concerned the results proved disappointing, for there are unknown factors which complicate the problem, for instance, the amount of erepsin in the intestinal juice used for activating the pancreatic secretion. Nevertheless, a point of some interest came out as a side issue; the edestin used contained 2·3 per cent. of tyrosine and 16·5 per cent. of glutamic acid. These substances were estimated in the digests, and the yield of tyrosine was 2·2 to 2·3 in all cases. The yield of glutamic acid was never so high as 16·5, but varied from 3 to 11·5. This shows that digestive enzymes are able to liberate certain amino-acids from the protein complex more readily than others, and it should be added that tryptophan as well as tyrosine is wholly set free within a few hours. Similar results were obtained when casein was used instead of edestin (Abderhalden and Voegtlin[9]). The rate of protein cleavage varies very considerably under the influence of different enzymes; it is well known, for instance, how greatly the velocity of the action is increased by trypsin in comparison with pepsin. The rate is still slower in the case of autolytic ferments. Even after fifty days' digestion in the case of the liver, complexes giving the biuret reaction were still present, and only a little more than half the quantity of cleavage products were obtained which are formed by hydrolysis with hydrochloric acid (Abderhalden and Prym[10]). Curiously enough the presence of blood in an organ lessens the rate of autolysis (Preti[11]). The inferiority of the stomach's action was also demonstrated in the case of the polypeptides, diglycyl-glycine and triglycyl-glycine ethyl ester (the biuret base); whereas these substances are rapidly broken up and absorbed in the intestine, any similar action of the gastric juice in dogs is minimal or absent (Abderhalden, London, and Voegtlin[12]).

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[5] *Abstr.*, 1907, i, 665.

[6] *Ibid.*, 666.

[7] *Ibid.*, 996.

The most interesting work on the cleavage of polypeptides which Abderhalden and his colleagues have produced is the discovery that the red corpuscles and platelets of the blood possess the power of breaking them up, glycyl-*l*-tyrosine being the dipeptide mainly employed (Abderhalden and Deetjen[13]). The investigation of other cells is in progress, as also is the question whether

[8] *Abstr.*, 1907, ii, 893.
[9] *Ibid.*, 893.
[10] *Ibid.*, 897.
[11] *Ibid.*, 897.
[12] *Ibid.*, 892.
[13] *Ibid.*, 889.

the higher polypeptides and proteins are decomposable in the same way. White blood corpuscles have not yet been obtained in sufficient quantity, free from other formed elements, in order to test the question on them, but lymph cells obtained from the thoracic duct and pus cells were found to have little or no action. Turning to the fluid part of the blood, Abderhalden and Oppler[14] found that the plasma and serum do not produce that cleavage of glycyl-*l*-tyrosine which the coloured corpuscles and platelets bring about so readily. A large number of other dipeptides were investigated with the same negative result, the only case where cleavage occurred being that of *dl*-alanyl-glycine. Tri- and tetra-peptides were, however, decomposed by the plasma, and this action cannot be due to enzymes absorbed from the intestine, for both trypsin and erepsin are capable of splitting glycyl-*l*-tyrosine easily. Truly, of the multiplication of ferments there seems no end. These investigations were made on horses' blood chiefly and they led Abderhalden and Rona[15] to perform similar work on human blood-serum. This fluid was obtained from thirty cases of disease; in eleven there was a slight cleavage of glycl-*l*-tyrosine; in the remainder there was none. In a few cases the urine was also investigated, but always with negative results; the number of observations, both on blood and urine, is admittedly too small at present for definite conclusions, useful to the pathologist and clinician, to be drawn.

Digestion and Absorption.

Experiments on Dogs.—The difficulty of studying digestion and absorption in the living animal is an obvious one, but the surgical ingenuity of Pawloff enabled him to make fistulous openings in different parts of the alimentary canal, and yet to keep his dogs alive for prolonged periods in an approximately normal state. This method has been elaborated by London, and he has now in his possession a number of dogs so operated upon that they are available for experiments of the kind indicated. His numerous writings have rendered even the names of his dogs familiar to the readers of Hoppe-Seyler's *Zeitschrift*, in which he publishes his papers. Food can be administered, and the stage of digestion reached in any segment of the alimentary tube can thus be ascertained, as well also as the amount of absorption which has occurred. I shall not attempt even to summarise these numerous papers, but a better plan will be to take one or two definite examples of the sort of work which is possible under these new conditions, and I will start with a simple instance on the absorption of alcohol; it was found that this substance is absorbed throughout the alimentary tract; in the mouth, naturally, the absorption is minimal; about 20 per cent. is absorbed from the stomach, 8·7 per cent. in the duodenum, 53 per cent. in the jejunum, and 18 per cent. in the ileum (Nemser[16]).

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[14] *Abstr.*, 1907, ii, 889.

[15] *Ibid.*, 890.

Another piece of work performed by Levites[17] on the same dogs relates to the digestion of fats, especially with regard to the relative absorption of the products of fat cleavage. If stearic, palmitic and oleic acids are given the quantities absorbed bear the relationship 1 : 3 : 4 respectively. Under ordinary conditions of digestion most of the acids are saponified, and it was found that the absorbability of the sodium salts has the same relationship as, but is two and a half times greater than, that of the acids. All the glycerol is absorbed before the ileum is reached.[18]

Still more interesting results were obtained on the absorption of proteins and their cleavage products. If glycine *d*-alanine and *dl*-leucine are given by the mouth they are recognisable in the stomach for a long time; by far the greatest amount of these amino-acids, probably all, leave the stomach by the pyloric orifice, and in the duodenum absorption begins rapidly. In the lower segments of the intestine they have entirely disappeared (Abderhalden, Prym, and London[19]). The relative unimportance of the stomach[20] as an organ of absorption was shown in experiments in which meat was given; no absorption of nitrogen occurred in the stomach, and this confirms previous researches in which white of egg and bread were administered (London and Polowzowa[21]). The course of digestion and absorption was followed by feeding the animals on a definite protein (gliadin), and the issuing chyme from different regions was collected and analysed; the rapid absorption of amino-acids noted in previous work was confirmed, and an interesting point was the identification of dipeptides, although it is doubtful whether these were precursors of the amino-acids or formed from them (Abderhalden, von Körösy, and London[22]). More complicated problems are dealt with when mixed diets are given, and I will conclude my references to this branch of work by dealing with one of these. The course of events was followed

[16] *Abstr.*, 1907, ii, 894.

[17] *Ibid.*, 891.

[18] Compare v. Fürth and Schütz (*Abstr.*, 1907, ii, 976). The results obtained do not correspond with those above stated, but the method used was to employ isolated loops of intestine, which is a more artificial condition.

[19] *Abstr.*, 1907, ii, 892.

[20] It is only fair to mention that Salaskin (*Abstr.*, 1907, ii, 281) criticises London's methods, which he regards as too complicated for the deduction of correct physiological conclusions. He further believes that absorption of nitrogenous substances occurs in the stomach; I cannot myself endorse either of these views.

[21] *Abstr.*, 1907, ii, 894.

[22] *Ibid.*, 893.

as before in one series when a pure protein (gliadin) was given, and in another series when this was mixed with fat. The gliadin disappears from the stomach into the intestine either with or without fat admixture four hours after the meal, whereas at the same time only 41 per cent. of the fat has passed on. But on examining the state of matters an hour earlier it was found there had been marked delay on the onward journey of the protein if fat was also present. This "sorting out" action of the stomach, which has been denied by some observers, opens up the interesting question whether this may not after all be an important part which the stomach plays, and so some light is thrown upon what we have already referred to as the obscure subject of the real use of this organ.

Further light has been shed on the question by an important piece of work carried out by Cannon[23] in the Harvard Laboratory. He entitles his paper very appropriately, "The Acid Control of the Pylorus." In order that the processes occurring in the stomach may advance in an orderly manner it is necessary that the food should be retained in it until the acid which is secreted only in its cardiac half should be thoroughly mixed with the food, and therefore until the portions of chyme in the pyloric portion are acid. The processes in the duodenum likewise require that the food shall be checked by the pyloric sphincter until it is acid, otherwise it will not stimulate the so-called duodenal reflex, which is in reality the formation of the chemical stimulus (secretin of Bayliss and Starling) for the flow of bile and pancreatic juice. The stomach accordingly is emptied by occasional discharges into the duodenum, the control being exercised by the condition of the pyloric sphincter. It is therefore necessary to explain the intermittent action of this muscular ring, and it is found that acid in the antrum opens the pylorus, and acid in the duodenum closes it; because the acid in the duodenum is soon neutralised, the closure of the pylorus is intermittent. That acid in the antrum is the signal for opening is indicated by the following evidence:—(1) If carbohydrates are moistened with sodium bicarbonate, their normally rapid exit from the stomach is delayed; (2) if proteins are moistened with acid, their normally slow exit is hastened; (3) the introduction of acid into the antrum through a fistula causes pyloric opening; and (4) in an excised stomach kept alive in oxygenated Ringer's solution, the pylorus is opened by acid on its gastric side. That acid in the duodenum keeps the pylorus closed is shown by the following evidence:—(1) Acid introduced into the duodenum inhibits gastric discharge, not by stopping peristalsis but by closure of the pylorus; (2) if the pancreatic and bile ducts are tied and so neutralisation of the acid chyme by alkaline fluids prevented, the stomach empties more slowly than under normal conditions; and (3) the discharge of protein becomes rapid if the pylorus is sutured to the intestine below the duodenum, or if a ring is cut through the muscular coats immediately beyond the pylorus. This last experiment shows that the effect from the duodenum is a local reflex action, mediated, like the movements of the small intestine, by the plexus of Auerbach.

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[23] *Abstr.*, 1907, ii, 974.

Metabolism.

From a study of digestion and absorption it is an easy and logical step to pass to questions of the manner in which food-stuffs are utilised and finally disposed of through excretory channels.

Nutritive Value of Protein Cleavage Products.—Abderhalden and Rona[24] have published a research which confirms the work already performed by Loewi and others, that the abiuretic cleavage products of protein are capable of maintaining nitrogenous equilibrium. A growing dog was fed on these materials with good results. In this paper also they discuss the seat of protein synthesis, and arrive at the general conclusion that the main place where it occurs is the intestinal wall. They base this conclusion principally on the fact that they were unable to discover the amino-acids in the circulating blood during the course of absorption. They guard themselves by admitting the difficulty of detecting small quantities of such substances in the blood, and the possibility that the tissue cells generally can build up their protein from simple crystalline materials is not denied.

This is a question which I entered into in last year's Report (Vol. III., p. 234), and the conclusion there reached was that proteins are absorbed as amino-acids, and that evidence of any special synthetic formation of proteins by the epithelium of the intestine is lacking; the greater part of them are never built into living protoplasm at all, but they are rapidly converted by the liver into urea, and this finds an easy exit from the body by the urine. Abderhalden and Rona's paper revives the whole controversy once more, and it is therefore necessary to examine their conclusion a little more thoroughly. We may freely grant their general trustworthiness as analytical chemists; nevertheless, it is always a dangerous practice to draw conclusions from negative results; they, moreover, take no notice of the work of others who have succeeded in obtaining positive evidence of the presence of amino-acids in the blood during absorption.

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[24] *Abstr.*, 1907, ii, 892.

If we accept their dictum that amino-acids are never found in this situation, we are also bound to the view that all the cleavage products of protein cleavage are resynthesised into protein, and this is a conclusion which is directly contrary to the great mass of experimental evidence. The whole trend of modern work on metabolism shows that quite a small fraction of the products are ultimately utilised in this way, and that by far the greater part of them undergo exogenous metabolism and are discharged as urea without having been built into protein molecules at all.

Many years ago Kühne argued that the amount of amino-acids in the intestines is so small at any particular moment that complete protein cleavage cannot be considered to occur to any great extent. He lost sight of the fact that the amino-acids were not formed for the purpose of accumulating there, but for absorption. So with amino-acids in the blood, they are not absorbed in order to be stored in that fluid, but are removed from it by the tissue cells and dealt with there, either for the purpose of assimilation into protoplasm or for discharge as waste material by the kidney. It is only necessary to suppose that this occurs very rapidly, and this (together with the admitted difficulty of detecting small amounts of amino-acids in the blood) will fully explain Abderhalden and Rona's negative findings. There is evidence that metabolic exchanges must occur with great rapidity. The blood does its work while it is in the capillaries when the velocity is slow and the vessel walls sufficiently thin for the transference of materials in one or the other direction. It must, however, be remembered that the total length of capillary vessels through which any given portion of blood has to pass does not exceed from 1/50 to 1/30 inch (0·5 mm.), and, therefore, the time required for each quantity of blood to traverse its own appointed portion of the general capillary system will scarcely amount to a second. It is during this time that the blood does its duties in reference to oxygenation and nutrition, and the shortness of the time allowed shows the extraordinary rapidity of the exchanges which is necessary.

Abderhalden's reactionary conclusion on the matter shows a lack of the acumen which is usually noticeable in his writings, particularly as another of his pieces of research ought to have guarded him from such an erroneous explanation of his results. I refer to that on the behaviour of *d*-alanine in the organism of the dog which he undertook in co-operation with Gigon and London.[25] He actually injected a large amount of this amino-acid into the blood stream, and after the lapse of a short time attempted to find it there. Mixed with blood *in vitro* 3·43 out of 4 grams were recovered by the ester method; but mixed with the blood *in vivo* only a minute fraction was recoverable twenty minutes later. Now if, after the injection of a massive quantity of amino-acid like 8 grams into the circulating blood, from 98 to 99 hundredths disappear in a few minutes, is it surprising that in the more gradual process of normal absorption it is difficult or without luck even impossible to separate out from the circulating fluid a measurable quantity of such substances?

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[25] *Abstr.*, 1907, i, 891.

Nutritive Value of Gelatin.—The exact value of gelatin as a "protein sparer" is an old problem which is ever cropping up, but upon which Murlin[26] has recently done some exact work on dogs and on human beings; the sparing action of carbohydrates was found to be an important factor in obtaining high replacements. The sparing action of gelatin is, however, not due to any dextrose to which it may give rise, but owing to its containing substances which are nitrogenous. Its principal amino-acid (glycine) can be retained temporarily in the body, and this may serve to explain the high replacement of other proteins by gelatin; but even with abundance of carbohydrate food it is not retained permanently.

Metabolism of Glycine.—The question whether glycine can be formed in the organism *de novo* is answered in the affirmative by Magnus-Levy.[27] Benzoic acid was given to cream-fed rabbits and to starving sheep; the output of glycine (as hippuric acid) was found to be much greater than the amount which could have been contained in the body proteins used up during the experiment. The possibility that the excess of hippuric acid in these experiments was formed by the oxidation of higher benzoylated amino-acids led to the subcutaneous administration of these acids to rabbits and dogs, but in all cases the benzoyl derivatives passed unchanged into the urine; in contradistinction to these, formylglycine and formyl-leucine were broken down in the body.

Prolonged Protein Feeding.—D. Forsyth[28] has shown that the bad effects which Chalmers Watson described as following the prolonged feeding of birds on excess of protein food were really due to lack of lime salts. If lime salts are supplied in due amount the ill results (on bones, thyroid, and other tissues) do not occur.

Inanition.—Going to the other extreme, attention must next be drawn to the very complete investigation Cathcart has carried out on a professional fasting man. The details are too lengthy to be repeated here, but they relate to both organic[29] and inorganic[30] materials.

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[26] *Abstr.*, 1907, ii, 793, 895. Compare also Rona and W. Müller (*Abstr.*, 1907, ii, 186), who find that the addition of tryptophan and tyrosine do not increase the sparing action of gelatin.

[27] *Abstr.*, 1907, ii, 977.

[28] *Ibid.*, 635.

Uric Acid.—Dealing next briefly with some of the more important excretory substances, uric acid is usually one which claims its quota of papers. The past year forms an exception to the rule, the only important work being that of Leathes.[31] The excretion of this substance manifests a diurnal variation, being greater in the day than in the night. This is not a sign that the kidney is less active at night, for the excretion of total nitrogen is as high as or even higher than during the day time. In fever there is a rise in the excretion of most nitrogenous catabolites, but the increased output is most marked in the case of uric acid and least in the case of creatinine, which is a substance that Folin regards as a measure of tissue metabolism (as opposed to exogenous nitrogenous metabolism), and which, furthermore, remains constant in quantity in spite of variations in the food.

The purine bases of the urine are also increased during fever, and the experimental administration of xanthine or caffeine to monkeys will cause a rise in the body temperature. Sodium salicylate given simultaneously will prevent the rise in temperature. As A. R. Mandel[32] states, it would be interesting to determine whether xanthine forms a compound with salicylic acid analogous to diuretin (=caffeine+salicylic acid) thereby rendering it innocuous. It is not quite clear from Mandel's work whether the increase of xanthine and similar substances are to be regarded as the cause or the effect of a febrile condition; he appears to take the former view.

Creatine and Creatinine.—If the popularity of uric acid as a theme for research is on the wane, that of the substances mentioned at the head of this paragraph is in the ascendant. This is mainly due to the stimulus afforded by Folin's views, and also to the ease by which they can now be estimated by Folin's colorimetric method. It is not many years ago since it was believed that the muscular creatine was ultimately discharged as urea, and that the creatinine in the urine was mainly of exogenous origin from the creatine of flesh foods. Owing to the introduction of more exact methods present teaching is almost exactly the reverse of this; there is no evidence that the creatine of the body is a precursor of urea, in spite of the ease with which the transformation occurs in the test-tube. The injection of creatine into the circulation leads to no increase of the urea excreted by the kidney. Whether creatine so administered raises the creatinine output in the urine is also extremely doubtful. If large doses of creatine are given much is excreted as such, the rise in urinary creatinine being insignificant. Creatinine appears thus to be almost entirely of endogenous origin, and, as already stated, Folin regards it as one of the principal measures of tissue metabolism. Its absolute amount in the urine is remarkably constant, in spite of variations in the diet, although differences are noticeable in different people and different animals. Muscular work also produces no alteration in the amount secreted unless the work is very excessive and performed upon an insufficient supply of fatty and carbohydrate food. The following is a list of the principal papers on the subject during 1907. Grindley, Woods, and Emmett,[33] using Folin's method, have made accurate estimations in meat and meat extracts of various kinds. Among other points they have finally disposed of the statement made some years ago by G. S. Johnson that creatinine is the more abundant base of the two. Urano [34] also has performed similar determinations; the mean amount of creatine in muscle is 0·4 per cent., so that an average-sized man will have in the muscles of his body from 90 to 100 grams, a figure which brings home to one the quantitative importance of this substance. Creatine is easily dialysable, yet it does not dialyse out into the blood during life or into water when the muscles are removed from the body. Given with the food it is largely retained in the body, and so Urano concludes with Folin that the muscular protoplasm has the power of fixing it.

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[29] *Abstr.*, 1907, ii, 633.

[30] *Ibid.*, 794. See also similar experiments on dogs by Wolf (*Abstr.*, 1907, ii, 634, 794), and "Metabolism in a Healthy Vegetarian," by Little and Harris, *ibid.*, 486. See also F. G. Benedict's book on *Inanition Experiments on Man*, recently issued by the Carnegie Institution.

[31] *Abstr.*, 1907, ii, 114, 376.

[32] *Ibid.*, 1908, ii, 54.

K. O. af Klercker [35] confirms Folin's views on the whole, but goes a little further when he states that any biological relationship between creatine and creatinine, which are so closely related chemically, is questionable. He finds also that if the two bases are introduced into the blood stream both are excreted unchanged, and of the two creatinine is the more readily eliminated. He regards the relationship of the urinary creatinine to muscular creatine as unproved, though here he probably goes too far, for there is certainly some correspondence between the amount of muscle and the amount of creatinine; this is shown, for instance, by E. I. Spriggs's [36] investigation of a case of pseudo-hypertrophic muscular dystrophy, in which a reduction in the muscular tissues was accompanied by a sinking of the creatinine output, and also by Amberg and Morrill's [37] observations on new-born children; here the constancy of the creatinine excretion is as marked as in adults, but the total output is only about one-third of that in the adult, and this they connect with the smaller amount of muscular tissue in the child. Dorner[38] finds that inanition has no effect on the excretion of creatinine, and makes the interesting discovery that in this condition creatine itself passes into the urine. This again points to the breakdown of muscular tissue as a source of both bases. He injected experimentally several bases, and with some obtained a rise in creatinine excretion, in other cases there was none, and he finally suggests the possible origin of creatinine from nuclein.

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[33] *Abstr.*, 1907, ii, 187; 1908, ii, 53.
[34] *Ibid.*, 1907, ii, 111.
[35] *Ibid.*, 186.
[36] *Ibid.*, 377.
[37] *Ibid.*, 799.

Gottlieb and Stangassinger's[39] work on the subject deals mainly with autolysis; creatine is formed during the autolysis of muscle and other tissues; then it is in part transformed into creatinine by enzyme action, and finally both bases are destroyed; this action is attributed to enzymes, which they call creatase and creatinase respectively. Similar changes are also asserted to occur in the urine. No doubt physiologists will await further evidence before they regard the existence of these ferments as proved.

The only other paper I will refer to in this connexion is by Dakin,[40] and this deals with another aspect of the ferment question; he and Kossel were the discoverers a few years back of arginase, the enzyme which splits arginine into urea and ornithine. Dakin now finds that this ferment is a specific one for the exclusive hydrolysis of *d*-arginine or of substances containing the *d*-arginine grouping. Creatine and other guanidine derivatives structurally similar to arginine are not hydrolysed by this enzyme.

Other Bases in Meat Extracts.—Kutscher[41] has been diligently exploring this neglected corner of the physiological field, and has discovered a number of new bases, in addition to others which, like creatine, creatinine, choline, and neurine, were known previously. The new bases are labelled with quaint names, such as ignotine,[42] novaine, carnitine, vitiatine, &c., a fact which in itself reveals how scanty is the present knowledge of their chemical composition. The good effects of beef-tea as a stimulant in disease are well known; its harmful action, however, is not yet so widely recognised by the medical profession, and yet this is very marked in certain pathological conditions; no doubt some of the bases alluded to are the toxic agents. A preliminary investigation with a view to determining this more accurately has been published by Slade,[43], but the deductions as to which constituents the powerful action of meat extracts is due are put forward with reserve. In moderate doses the heart's rate and force are increased; this is not due to creatine, xanthine, or urates; the increase in the movements of plain muscle all over the body is probably produced by ornithine and novaine; the agents concerned in causing diuresis, purgation, and other symptoms are quite unknown.

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[38] *Abstr.*, 1907, ii, 709. Benedict and Myers (*Abstr.*, 1907, ii, 492) and Cathcart (*loc. cit.*), in their work on inanition also found creatine in the urine.

[39] *Abstr.*, 1907, ii, 637. Seemann (*ibid.*, 490) found that the increase of creatinine in muscular autolysis is specially great if a protein rich in arginine, such as gelatin, is added also.

[40] *Abstr.*, 1907, i, 1099.

[41] *Ibid.*, 264; ii, 569, 708.

[42] Probably identical with carnosine (Gulewitsch, *Abstr.*, 1907, i, 264).

Lactic Acid.—This is the most important of the non-nitrogenous catabolites in muscle, and the only one I shall touch upon. Here again we are on much-traversed ground, but Hopkins and Fletcher's[44] treatment of the subject is by no means hackneyed, for they have been successful in discovering the reasons for so much disagreement between past observers. Working with frog's muscles they find that fresh resting muscle yields very small amounts of the acid, but this amount is increased by injuries of various kinds produced by mechanical means, heat, immersion in alcohol, and even by handling. The small amount of the acid found in fresh muscle is probably due to unavoidable manipulation. It is easy to see how neglect of this point has led to discrepancies in previous statements. For the actual methods used and the new facts elicited the original paper must be consulted; the somewhat lengthy abstract I presented when the paper appeared quite inadequately represents its importance; perhaps the most interesting of the discoveries recorded is that an atmosphere of pure oxygen prevents the survival development of the acid.

Tissue Respiration.—The rôle that oxygen plays in vital phenomena is a subject that I have treated in previous reports, and the obscurity surrounding this fundamental problem led the British Association some years ago to appoint a committee to deal with it. Previous to this time we were almost completely ignorant even of the amounts of oxygen used by various structures in conditions of rest and activity, mainly on account of the difficulties attendant on the estimation of blood gases. But the new and simple methods introduced by Haldane and Barcroft render the estimation even in small quantities of blood perfectly easy to-day, and in various laboratories throughout the country data are being accumulated in relation to this most important investigation. As an example of the results obtained, we may take the work of Barcroft and Dixon[45] on the mammalian heart. The circulation of blood was maintained through the excised hearts of dogs and cats by perfusion from a living animal, clotting being prevented by the administration of hirudin; the gases were determined in the entering and issuing blood while the heart was in various conditions, rate, amplitude, and tonus being taken into account. The amount of oxygen taken up by the heart varies directly with its activity; the output of carbon dioxide varies in the same way but lags somewhat behind it. The output of carbon dioxide varies also with the rate of flow through the coronary vessels, and the interesting suggestion is thrown out that the vaso-motor changes in these may be controlled by the metabolic products of which carbon dioxide is the chief. Be this as it may (and in view of the doubts expressed in some quarters as to whether the coronary vessels possess effective vaso-motor nerves, it is well to withhold judgment on the question), the figures obtained are full of interest; they show that cardiac, like voluntary muscle, is of lower metabolic value, weight for weight, than secreting organs such as the kidney, pancreas, and salivary glands. In the resting organs the pancreas uses 0·03 to 0·05 c.c. of oxygen per gram per minute, the submaxillary gland 0·03, and the kidney 0·03. The figures for the feebly-acting heart are about one-third of these. When the organs are fully active the figures all rise, but the heart varies least, the highest figure obtained for the dog's heart being 0·083 c.c.

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[43] *Abstr.*, 1907, ii, 379. [44] *Ibid.*, 373. [45] *Ibid.*, 366.

Vernon[46] has studied the subject on the kidney perfused with oxygenated saline solution; the initial gaseous metabolism, which at first is as great as in the living animal, rapidly dwindles. In the course of the experiment the tissue proteins are dissolved out by the perfusing liquid without affecting the tissue respiration, and from this observation the conclusion is drawn that tissue respiration is associated with non-nitrogenous side chains of Verworn's "biogen" molecules. This may be so, but Vernon's experiments do not prove it, for the amount of protein washed away from the kidney cells whilst they remain alive can only be a small fraction of the total present.

Metabolism in the Embryo.—Abderhalden and Kempe[47] estimated tyrosine, glycine, and glutamic acid in eggs in various stages of incubation, but the changes found were so slight that inferences as to the possibility of one amino-acid being changed into others could not be drawn.

Lochhead and Cramer[48] found in rabbits that at an early date in development the maternal placenta contains a large store of glycogen; later on this decreases, and the decrease corresponds with an increase of the same substance in the fœtal liver. Since the introduction of Pflüger's exact methods of glycogen estimation several observers have expressed doubt regarding Claude Bernard's well-known statement on the richness of all fœtal tissues in glycogen. The latest to do so are Mendel and Mitchell[49]; a high percentage of glycogen is not characteristic of embryonic tissues; the liver, however, does not in the pig assume its glycogenic functions early. They, moreover, regard glycogen simply as a store of nutrient energy rather than, as Creighton thought, a peculiar mark of histogenesis.

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[46] *Abstr.*, 1907, ii, 111. [47] *Ibid.*, 896. [48] *Ibid.*, 370.

In their chemical studies on growth, the same observers have investigated two other questions, namely, inverting ferments and purine metabolism. They find that inverting ferments appear early in the embryonic intestine, so contrasting with ferments which produce protein-hydrolysis. In the embryo pig, maltase and lactase are present, but sucrase does not appear until after birth; lactase is, however, found in certain portions only of the intestine. In birds, lactase is never found, but sucrase is present in the newly-hatched chick as well as in the adult hen.

In reference to purine metabolism they find that the nucleic acid of the embryo pig's liver yields only two purine substances, namely, adenine and guanine. Nuclease and adenase are present, but guanase is absent as in the adult pig, although the other viscera yield it at an early date. Oxydases and the uricolytic ferment are not developed until after birth. A very similar investigation with corresponding results has also been published by Jones and Austrian.[50] In their previous work they have shown that the distribution of the nuclein ferments (guanase, adenase, and xantho-oxydase) differs in different animals, and now they have found that it also differs in the same animal in different phases of its development; thus in the liver of early pig embryos all these enzymes are absent; a little later adenase makes its appearance and then xantho-oxydase, guanase being absent as it is in the adult.

Chemistry of Nervous Tissues.

The Detection of Choline by Chemical Methods.—For some years past Mott and I have laid special stress on the importance of the discovery of choline in the circulating fluids as a definite proof of the breakdown of nervous tissues, and our expectation that its detection would be useful in diagnosis has already been fulfilled. Allen and French in this country and Mansfeld in Germany pointed out that the chemical test with platinic chloride may lead to confusion, since the chlorides of ammonium and potassium when treated with platinic chloride give rise to crystals which are liable to be mistaken for the platinichloride of choline on mere inspection. A chemical test is obviously best for clinical work in

[49] *Abstr.*, 1907, ii, 895.

[50] *Ibid.*, 708.

which, as a rule, only small quantities of cerebro-spinal fluid or blood are available; a clinical observer also has usually neither the time nor the opportunity of applying any further tests to crystals he is observing. It was therefore necessary to seek for other tests for choline which are not given by the inorganic chlorides. As a result of O. Rosenheim's search in this direction, he succeeded in discovering three.[51] One of these is a colour reaction with alloxan; the second is the formation of a characteristic red precipitate with potassium bismuthoiodide, and the third is a modification of the iodine reaction. This third test, being the most characteristic and readily applicable to clinical uses, is the only one I shall describe in full here. The yellow crystals of choline platinichloride are prepared from the alcoholic extract in the usual way, and to these a strong solution of iodine in potassium iodide is added. The crystals alter in a characteristic way, and the change can be watched with the microscope. In the course of a few minutes the yellow octahedral or prismatic crystals disappear and their place is taken by dark brown plates and prisms in large quantities which show marked dichroism, are doubly refracting, and have a superficial resemblance to the well-known hæmin crystals. They are composed of choline periodide ($C_5H_{14}ONI_9$), but are extremely unstable, and if the slide is allowed to stand so that the liquid gradually evaporates the crystals begin to disappear and their place is taken by brown, oily droplets; this indicates the formation of a lower iodide. If now a fresh drop of the iodine solution is added the crystals gradually form once more, and their formation and disappearance can be watched repeatedly. If ammonium or potassium platinichlorides are present on the same slide they remain unchanged under the action of the iodine solution.

Donath[52] has also described another distinctive character of the crystals of choline platinichloride; namely, they are doubly refracting, whereas the platinichlorides of ammonium or potassium are not. Rosenheim has confirmed this statement, and in some cases has made out another fact which is not devoid of significance. If he obtains from a case of pathological cerebro-spinal fluid a slide of the mixed platinichlorides and places it in the field of the polarising microscope the inorganic platinichlorides exhibit no double refraction, but a large proportion of the crystals present show the phenomenon. If he then subjects the slide to his iodine test many of the doubly refracting crystals are transformed into the brown crystals of choline periodide, and others yield crystals of different form from these and therefore consist of other platinichlorides, probably of organic nature, although they have not yet been identified. This is only what one would expect; the chemical structure of nervous material is so complex that the cleavage products liberated during the degenerative process must be numerous. The importance of the detection of choline arises because it is at present the only one of these numerous substances which can be identified with certainty and which can be detected with comparative ease. Its presence indicates the breakdown of one of the most abundant and best known of the constituents of nervous matter (lecithin), but suggests that it must be accompanied by the presence of numerous other similar and even dissimilar compounds.

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[51] *Abstr.*, 1906, ii, 133.

[52] *Ibid.*, 133.

In Rosenheim's [53] most recent paper on the subject he gives the results of his examination of numerous specimens of blood and cerebro-spinal fluid from cases of nervous disease, and also points out that the procedure of testing may be shortened by applying the iodine reaction direct to the alcoholic extract of the suspected fluid without the necessity of preparing crystals of the platinichloride first.

I had, happily, kept a considerable number of the preparations of crystals which Mott and I made years ago, and from which we drew our previous conclusions. On examining these afresh by the new means of identification we now possess I found that they do not consist wholly of the choline compound, but contain a considerable admixture of inorganic platinichlorides, especially the potassium salt. We, however, still hold that the obtaining of a large crop of crystals, whether they be those of the choline salt or of a mixture of the potassium and choline salts, is diagnostic of extensive breakdown in nervous tissues. The contrast between such cases and the insignificant yield from normal fluids is most striking. This is intelligible when we take into account the high percentage of potassium that, according to the work of Macallum and of Macdonald, nervous tissues contain. Some preliminary experiments indicate a considerable increase of the potassium in those cases of disease where disintegration of nervous tissues has occurred and where choline is also discoverable.

The Physiological Test for Choline.—Although the chemical test for choline is the one most suitable for clinical work, the physiological effect which choline exercises on blood-pressure is not devoid of interest. Swale Vincent in his earlier work on the physiological action of extracts of nervous tissues found that the intravascular injection of such extracts caused in anæsthetised animals a considerable fall of arterial pressure. I published simultaneously the same result, and attributed the fall to the presence of choline. Vincent, however, denied that choline was present. Subsequently, with Cramer, he amended this statement, and then said that the choline present was in the form of dicholine anhydride. The existence of this compound is very problematical, and the analytical evidence presented is not very convincing; still, the suggestion that compounds or modifications of choline may exist in the body is not entirely unwarranted. Vincent and Cramer also found what I had missed, namely, that there are other substances present in such extracts which are readily soluble in ether and which produce a much more powerful depressor effect on the blood-pressure than choline, and that in the case of such substances the effect is not abolished by the administration of atropine (as that of choline is). They did not attempt to identify these materials; it is quite possible that they are absolutely distinct from choline; the view is also permissible that they are derivatives of choline. This second view gains point from a study of some experiments which Reid Hunt and Taveau brought forward at the meeting of the British Medical Association in Toronto last year.[54]

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[53] *Abstr.*, 1907, ii, 637.

They have prepared and studied the physiological action of as many as nineteen compounds of choline, and they suggest the possibility that some of these may be formed in the body. Some of them are more and others less active than choline itself; the most powerful is acetylcholine; this is one hundred times more active in producing a fall of blood-pressure than adrenaline is in producing a rise; the injection of a few c.c. of a solution containing it, diluted with one hundred million times its volume of water, produces a distinct effect in a rabbit. The action of acetylcholine is not annulled by atropine, and it is capable of overcoming the effect of adrenaline. On the other hand some of the choline derivatives examined are less powerful than choline; the introduction of a phenyl group, for instance, diminishes its depressor effect.

As an outcome of his work Reid Hunt recommends two new tests for choline; one is the formation of the acetyl compound to render the physiological test more sensitive; the other is the formation of the benzoyl compound; this gives a distinctive crystalline platinum salt which cannot be confused with the platinichlorides of ammonium or potassium. I think that in the future those engaged in research will have therefore no lack of methods to render the detection of choline a matter of no difficulty.

Several observers have surmised that the breakdown of lecithin in the body is due to the activity of a ferment, although hitherto attempts to isolate the enzyme have failed. Rosenheim in his latest paper just quoted has in his examination of certain nonnervous tissues for choline found it as a result of autolysis, although it is not present as such when the tissue is fresh. Marinesco[55] suggests that in peripheral nerves the ferment is formed by the neurilemmal cells which actively multiply during Wallerian degeneration, but this interesting hypothesis has not yet received any experimental confirmation.

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[54] *Brit. Med. J.*, 1906, II, 1788.

The Cholesterol of the Brain.—Cholesterol is an abundant constituent of nervous tissue, and this cannot be devoid of physiological importance, but at present we know nothing either of its mode of origin, its destination, or its function. It is usually isolated from the brain by extraction with ether, and subsequent precipitation of this ethereal extract with alcohol. But ether extraction of fresh brain is a troublesome operation; it swells up, and filtration and complete removal of the cholesterol is difficult and tedious. Baumstark[56] avoided some of these drawbacks by subjecting the brain to "ether dialysis," but the time required for this is from one to three months, and even then the extraction of cholesterol is incomplete. A second disadvantage is that ether dissolves not only cholesterol but large quantities of other substances as well, and the separation of cholesterol from these involves several operations and is incomplete. Baumstark only obtained 35 per cent. of the total cholesterol by this method; the rest is carried down with the precipitates of lecithin, &c., and can only be freed from them by saponification, a fact which led him to assume the presence of cholesterol-esters in the brain. Zuelzer[57] precipitated the phosphatides from their ethereal solution by acetone, and effected in this way a more complete separation.

It occurred, however, to Rosenheim[58] to use acetone as the extracting agent. This dissolves only cholesterol, and its use therefore enables one to obtain that substance readily and also facilitates the study and separation of certain other constituents of nervous material. It is, however, necessary to remove water first, and this is done quite simply by means of plaster of paris. The brain material is passed through a mincing machine and then mixed with sand and about three times its weight of plaster of Paris. In a few hours the mass sets hard, and this is easily broken up into a powder which lends itself readily to extraction with acetone at the ordinary temperature. The first extract usually contains some water and therefore less cholesterol; but from the second and third extracts the bulk of the cholesterol crystallises out in an almost pure condition on evaporation of the solvent.

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[55] *La Presse Medicale*, 16 Feb., 1907.

[56] *Abstr.*, 1885, 918.

[57] *Ibid.*, 1899, ii, 504.

[58] *Ibid.*, 1906, ii, 240.

Using this method, Miss M. C. Tebb[59] found that the extraction of cholesterol was complete, and no further yield occurred on saponification. Baumstark's idea that some of the cholesterol is free and most of it in combination is therefore incorrect. While Miss Tebb's work was in progress the same conclusion that cholesterol occurs in a wholly free condition in brain was reached by a different method by Bünz.[60] This observer paid special attention to melting-point determinations; the melting point is lowered when cholesterol and cholesterol ethers are mixed together. Miss Tebb did not, however, find the extremely great depressions which Bünz described. This, after all, is a small point of difference. The main conclusion is that by the use of trustworthy methods it has now been shown that cholesterol occurs as such in nervous tissues, and not in the form of cholesterol ethers or cholesterol esters.

Protagon.—This term was originally used by Liebreich in 1865 for a crystalline substance which can be obtained from brain by a simple process of extraction either with ether alone or with alcohol after preliminary treatment with ether. The same substance had, however, been obtained by practically the same method as early as 1834 by Couerbe, and by him designated cérébrote. Perhaps no substance of physiological importance has undergone so many vicissitudes as protagon; the pendulum of scientific opinion has here swung backwards and forwards, protagon being alternately regarded as a chemical individual and as a mixture of substances. The matter, however, is at last definitely settled once and for all. Protagon is a mixture, as Thudichum in 1874 was the first to prove, and the use of the term has now only a historical justification. A series of death-blows to protagon as a chemical unit has been struck in America by Gies and his colleagues,[61] and in England by O. Rosenheim and Miss Tebb.[62] A series of blows has been necessary, for protagon has died very hard and the most recent attempt to resuscitate it has been made by Cramer,[63] working in Liebreich's laboratory and later at Edinburgh in conjunction with Lochhead,[64] but the obvious fallacies of this work have been amply demonstrated by both the American and the English workers referred to.

Cramer has introduced a new method of preparing protagon which is very largely a reversion to Couerbe's original process, and he concludes "that the close agreement between the phosphorus percentage of various samples of protagon prepared by

[59] *Abstr.*, 1906, ii, 241.

[60] *Ibid.*, 1905, ii, 841.

[61] Lesem and Gies, *ibid.*, 1903, ii, 90; W. Koch, *ibid.*, 1902, ii, 676; Posner and Gies, *ibid.*, 1905, i, 54; Gies, *ibid.*, 1907, ii, 995.

[62] *Abstr.*, 1907, ii, 995.

[63] *Ibid.*, 1904, i, 462.

[64] *Ibid.*, 1907, i, 672.

diverse methods is strong evidence in favour of the view that protagon is an individual substance of a well-defined chemical composition." The term close agreement involves percentages varying from 0·97 to 1·5. But even if the agreement were still closer one might nevertheless be dealing with a number of substances mixed together in approximately the same proportion. Cramer has evidently not grasped the fact that the question at the root of the matter is not: Can products closely resembling the protagon of Liebreich and of Gamgee and Blankenhorn be prepared by new methods? But rather, is the product prepared by any of these methods a sample of a definite chemical individual?

Rosenheim and Miss Tebb, for instance, have prepared a substance with the properties of protagon by another new method, and yet their conclusion is the exact opposite to Cramer's. This new method briefly consists in removing water by plaster of Paris and then cholesterol by cold acetone as already described. Hot acetone then extracts protagon, and this is deposited in crystalline form when the hot solution cools. No doubt the fact that protagon shows a microcrystalline structure has influenced chemists in accepting it as a uniform chemical substance,[65] but the data on the other side are now too strong to allow this fact to overbalance them.

The workers in America and those in my own laboratory have approached the problem in somewhat different ways, but their conclusions are the same. As I am naturally more familiar with the work at King's College, and have seen the greater part of the experiments while in progress, I will be content with mentioning the grounds upon which Dr. Rosenheim and Miss Tebb base their conclusions; these are briefly as follow:—

1. Liebreich's, Gamgee and Blankenhorn's, and Cramer's protagon represent practically the same substance as Couerbe's cérébrote of 1834.

2. A similar substance can be obtained by the acetone method referred to.

3. All of these protagons resemble one another in microscopic appearance, and roughly in phosphorus percentage.

4. But all and each of them may be split into substances of widely varying phosphorus and nitrogen percentage by methods which involve no chemical breakdown, namely, by simple fractional crystallisation at different temperatures or with different solvents.

5. These products also show great differences in optical activity and in the amount of galactose split off by acid hydrolysis.

6. Protagon (with about 1 per cent. of phosphorus) is therefore

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[65] It has certainly influenced myself in previous writings on the subject.

not a definite chemical compound. It consists of a mixture of substances; some of these (such as phrenosin) are free from phosphorus and others (such as Thudichum's sphingomyelin) are rich in phosphorus.

7. The base called sphingosine by Thudichum, as well as choline, is found amongst the products of protagon-hydrolysis.

Cramer and Lochhead state that "the view that protagon is a mixture of substances . . . cannot be accepted until the substances constituting the mixture have been isolated."

With this statement all will be in agreement. It, however, implies that the substances have not been isolated, and so conveniently disposes of a great deal of work of those who from Thudichum onwards have attempted to obtain these substances in a pure condition. One such substance has certainly been isolated, namely, phrenosin under different names by various workers, including one who believed in the individuality of protagon (namely Gamgee, who called it pseudo-cerebrin). That we are less fully acquainted with the other substances is due to the circumstance that the investigation of the chemistry of the brain is surrounded by difficulties which can only be appreciated by those who have actually worked at the subject.

But since Dr. Rosenheim and Miss Tebb completed the paper I have given the substance of, they have continued to work at the separation of protagon into its main constituents and are at present engaged in examining and analysing them. The method employed is that of systematic fractionation by means of alcohol, chloroform, and acetone. The largest fraction (approximately 60—70 per cent. of the original protagon) comprises at least two crystalline substances which are nearly phosphorus free ($P=0{\cdot}09$). The quantity of phosphorus in the remaining substances (of which so far one has been obtained in crystalline form) amounts to about 3 per cent. It is evident that a mechanical mixture of these two substances in the above proportions would enable one artificially to reconstitute "pure protagon" with a phosphorus percentage of from 0·9 to 1·2. The details will, however, be published later.

Paranucleo-protagon.—This is the name given by Ulpiani and Lelli[66] to a compound in the brain in which they believe the protagon is combined; they state it can be resolved by alcohol into protagon and paranuclein. At the time this work was performed the idea that protagon is a chemical unit was held by most workers. Paranucleo-protagon is extracted from the brain by means of chloroform. Gies and Steel[67] have now shown that it, like protagon, is a mixture containing other substances besides the two mentioned

[66] *Abstr.*, 1902, ii, 573.

[67] *Ibid.*, 1907, i, 1097.

by Ulpiani and Lelli; probably, however, none of the constituents of protagon is really combined with a nuclein-like substance.

Sulphur in the Nervous System.—The sulphur compounds in nervous material have always attracted W. Koch in his work on brain chemistry, and his latest communication on the subject has only just been published.[68] He divides the sulphur-containing materials into four groups:—

(1) Lipoids, such as protagon. Although he does not believe in the entity of protagon, he suggests that its lecithin and cerebrin constituents are linked together by an organic sulphur radicle.

(2) Extractives soluble in 95 per cent. alcohol. These consist as to one-tenth of inorganic sulphates and the remainder of a taurine-like substance.

(3) Extractives soluble in water after previous extraction with alcohol and ether. These are principally inorganic salts, possibly mixed with a gelatin-like protein.

(4) Proteins, mainly globulin, neurokeratin, and nuclei-protein. Grey matter contains chiefly globulin, nucleo-protein, and neutral sulphur compounds. White matter contains a larger proportion of neurokeratin and lipoid sulphur.

Koch's work strikes one as being problematical and unfinished. His suggestion that the constituents of protagon are chemically linked together is supported by the flimsiest analytical evidence, and will do harm if it serves to bolster up the protagon heresy. His statement that lecithin is one of the constituents of protagon is wholly incorrect, and has been abandoned for many years from Gamgee onwards. A very similar criticism may be passed upon his suggestions regarding the physiological rôle played by the sulphur compounds. No one doubts the necessity for brain-function of an excess of free oxygen; but whether it is the sulphur-containing groups which are specially susceptible of oxidation is a matter on which we have no certain knowledge. It is important, of course, to have ideas of this kind even if they are ultimately found to be nothing more than crude guesses, for they furnish a stimulus to investigate the matter more deeply. The very remarkable disease called *Dementia præcox* is attracting considerable attention from alienists at the present day. Three cases of this malady came post-mortem into Koch's hands, and on the supposition that some of the symptoms could be explained by deficient oxidation in the brain he investigated the sulphur compounds; the lipoid sulphur was present in normal amount; the neutral sulphur was reduced by 35 per cent., and the inorganic sulphur was increased. It will probably be better at present to be content with pigeon-holing these scanty data and leave conclusions for a later year, when our knowledge is riper.

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[68] *Abstr.*, 1908, ii, 52.

Lecithin and Phosphatides in other Situations.—Although lecithin and other phosphatides have attracted special attention in the nervous system because of their abundance in that situation, it must be remembered that they are universally present in all living protoplasm. Thus the phosphatides of egg yolk are according to their solubilities separated by Stern and Thierfelder[69] into three groups, and a preliminary study of their properties is in progress.

A similar unfinished piece of work on the lecithin-like substances obtained from cardiac and voluntary muscle has been published by Erlandsen,[70] who finds that they differ in the kind of fatty acid they contain and in other particulars; he classifies them into monoaminomonophosphatides, diaminomonophosphatides, monoaminodiphosphatides, and diaminodiphosphatides.

The lecithin of bone marrow has been studied by Otolski[71] and by Gliken.[72] The paper by the former deals mainly with methods of separation; the lecithin found yields on decomposition choline, glycero-phosphoric acid, and unsaturated fatty acids. The paper by the latter is quantitative; the amount of lecithin is deduced from the phosphorus content of the ethereal extract. The amount of lecithin in the fat averages 2 to 4 per cent.; in horses it is lower (1·4 per cent.); the highest numbers were obtained in very young pigs (28 to 47 per cent.); speaking generally its amount diminishes with age.

The Possible Functions of Lecithin and Cholesterol.—The universal distribution of these two substances in all living protoplasm is a fact that has long been known. Lecithin has been recognised as an important constituent of food, and its administration in cases of malnutrition is stated to have been attended with good results. Its stimulating action on individual organs such as the excised heart has also been noticed.[73] The exact way in which it acts is still hypothetical, but a ray of light has entered from a very unexpected quarter, namely, a study of the action of snake venom. Preston Kyes was the first to discover that in the process of hæmolysis, which is one of the results of the action of snake poison, lecithin acts as the amboceptor anchoring the poison on to the cell it attacks. Adopting Ehrlich's hypothesis that the action of toxins is analogous to that by which the food-proteins are assimilated by living cells, one can deduce from this observation the possibility that lecithin may assist the assimilation of food materials beneficial to the organism as well as of those which, like snake venom, the organism would prefer to be untroubled with.

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[69] *Abstr.*, 1907, ii, 896.

[70] *Ibid.*, i, 371.

[71] *Ibid.*, 666.

[72] *Ibid.*, ii, 566.

[73] See Danilewsky, *ibid.*, 981.

It is three or four years ago since Kyes made his original statements on the subject, but his views have been fully confirmed, and further details of the action of toxolecithids worked out.[74] Hæmolysis, of course, is only one effect of certain poisons; it is probably, however, only a sample of what occurs in other cells and is far more readily studied than the changes in other cells are. It may be produced by purely physical agencies, as when water is added to red blood corpuscles; but what may be called fermentative hæmolysis is more interesting, because it is a process, as already stated, which runs on the same lines as the assimilation of food material. Neuberg and Reicher[75] regard both hæmolysis and agglutination as intermediate stages in lipolysis, and the importance of lecithin as an amboceptor accentuates this hypothesis. Noguchi[76] confirms this view, and further shows that neutral fats (such as triolein) may play the same part at any rate in some forms of hæmolysis and bacteriolysis.

One naturally speaks with caution in dealing with a new and striking hypothesis which has still to stand the test of time and further experiment; but as far as one can judge at the present stage it does seem to be definitely proved that lecithin, and possibly other fatty compounds, are important auxiliaries and possibly necessities in the ferment-like actions produced by toxins; we shall also be fairly safe in accepting Ehrlich's views on the analogy between the mechanism involved in the assimilation of toxic proteins and those which are non-toxic, and so the importance of lecithin during normal assimilation may be provisionally accepted. This has led us a long way from our starting point, the lecithins of the brain; it is quite possible that the large amount of these substances in nervous tissues may have some additional significance of its own there, or it may be that such actions as lecithin possesses in protoplasm generally may be specially called into play in the chemical exchanges which lie at the root of nervous activity.

Not only have the researches referred to been useful in clearing up some points in relation to the function of lecithin, but they have also thrown light on what is a still more obscure problem, the function of cholesterol. Here again, however, the enormous quantity of cholesterol in nervous tissues is strikingly different from what obtains in other organs of the body. Moreover, as we have already seen, the cholesterol of the brain is free; that of other tissues is probably in combination as esters; this, at any rate, is the case for the cholesterol of the blood.

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[74] See, during the present year, Morgenroth and Carpi on "Bee Poison," *Abstr.*, 1907, ii, 286; on "Cobra Venom," *ibid.*, 570; Kyes, *ibid.*, 569; Teruuchi, *ibid.*, 571.

[75] *Abstr.*, 1907, ii, 570.

[76] *Ibid.*, 890, 974. See also Liebermann, *ibid.*, 973.

Researches on the lines of immunity, such as have demonstrated the favouring action of lecithin, have shown that cholesterol has the opposite action, and it may therefore be that the normal function of this interesting member of the terpene group is a protective one, enabling the body cells to withstand the action of toxic agents. In support of this view we may quote the following:—

H. Pribram[77] showed that after feeding on cholesterol the percentage of that substance rises in the blood, and resistance to hæmolytic agents is increased. Morgenroth and Carpi[78] found that the hæmolytic action of a mixture of bee poison and lecithin is decreased by cholesterol. Pascucci,[79] in experiments with artificial blood corpuscles, demonstrated the protective influence of a covering membrane which contained cholesterol. Hausmann[80] obtained corresponding results when investigating the hæmolytic action of saponin. Hausmann went further than this and showed that in order that cholesterol may exercise this action the hydroxyl group and the double linking must be intact, and this has been confirmed by Abderhalden and Le Count.[81]

Glycogen, Sugar, Diabetes.

As one of the main practical interests of a study of carbohydrate metabolism is the condition in which that metabolism is upset, I make no apology for grafting my summary of the year's work on glycogen and related subjects on to a general account of diabetes.

The term diabetes doubtless includes many pathological conditions which all possess in common the symptom of glycosuria and usually of glycæmia also. In animals, the condition can be produced by diverse experimental means, of which it will be sufficient to mention the following:—

1. Diabetic puncture.
2. Extirpation of the pancreas.
3. Administration of phloridzin.
4. Administration of adrenaline.

1. *Diabetic Puncture.*—Claude Bernard made the discovery that injury to the grey matter in the floor of the fourth ventricle in the region of the vaso-motor centre leads to glycosuria. This form of glycosuria is of interest to the medical man, because brain

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[77] *Abstr.*, 1907, ii, 105.
[78] *Ibid.*, 286.
[79] *Ibid.*, 1905, ii, 729.
[80] *Ibid.*, 744.
[81] *Zeitsch. Exp. Path. Ther.*, 1905, **2**, 199.

disease in man, especially in the region of the bulb, is frequently associated with sugar in the urine. It cannot be regarded as of purely vaso-motor origin, since a dilatation of the abdominal vessels produced by other means is not accompanied by a diabetic condition. There are experiments recorded which show that the liver nerves have a direct influence on the liver cells quite apart from their influence on the blood-vessels; for instance, stimulation of the vagus and also of the cœliac plexus is stated to lead to diminution of the hepatic glycogen and a corresponding increase of sugar in the blood. It may be that puncture diabetes is due to injury to or stimulation of a centre controlling the action of this secretory nervous mechanism. J. J. R. Macleod[82] has recently investigated the glycogenolytic fibres, as he terms them, and finds them present only in the splanchnic nerves and not in the vagus if all precautions against the occurrence of asphyxia are taken.

The discovery of the "diabetic centre" gave rise to the erroneous idea that all cases of diabetes are of nervous origin; but injury to the centre is only effective in its results when the liver contains glycogen; puncture diabetes cannot be produced in an animal in which the store of glycogen has been depleted by fasting.

The transformation of glycogen into sugar is accomplished by a ferment (liver-diastase), and a series of interesting papers by Bang[83] have dealt with the amount of this ferment present under various conditions, the experiments having mainly been performed upon rabbits. Among other points, the influence of the nervous system on glycogen metabolism was investigated. The effect of a blow on the neck is to cause an increase in the liver-diastase, the liver enzyme being independent of the blood-diastase. Bernard's puncture diabetes is similarly produced; the primary stimulation is, however, followed by inhibition, and it is suggested that in physiological conditions, sugar production is a balanced action between stimulation and inhibition, and possibly the centres controlling the two actions are distinct. The efferent path for the nerves controlling this action in the liver is the sympathetic (this confirms Macleod's view just stated). It was, however, found that stimulation of the central end of the cut vagus produced glycæmia and glycosuria whether the liver contained much or little glycogen. This reflex diabetes, as it may be termed, is thus independent of the liver, and is believed to originate from the change of glycogen into sugar in the muscles of the body. The independence of the glycogenic function of the muscles, apart from that of the liver, is an old idea which has within the past year received support from de Filippi's[84] experiments on dogs with an Eck's fistula.

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[82] *Abstr.*, 1907, ii, 800.
[83] *Ibid.*, 487, 634, 900.
[84] *Ibid.*, 707, 794.

When the liver is thrown out of gear by this operation the animal is still able to utilise starch, and shows no sign of glycosuria on a moderate diet; still, it is found that quite small doses of some sugars (*e.g.*, lactose) will lead to their appearance in the urine, and the organism is absolutely intolerant to lævulose. The amount of hepatic glycogen is greatly reduced by the operation, but the amount in the muscles remains unaltered. This not only shows the independence (or it may be partial independence) of the two tissues in carbohydrate metabolism, but also explains how the latter can go on in spite of the diminution of hepatic activity.

In these various forms of nervous diabetes there is no fundamental disturbance of the power of the organism to burn and utilise sugar; there is simply a diminution or overstraining of the sugar-holding capacity of certain organs, and therefore they cannot be classed with diabetes mellitus in the strict sense. The same is true for what is called "alimentary glycosuria," which occurs when sugar is given in larger amount than the liver can deal with, and which is most readily produced when the metabolic functions of the liver are "below par." This, at any rate, is the usual view taken of alimentary glycosuria; de Filippi alone among recent writers feels doubtful whether it is a symptom of liver insufficiency, on the grounds that he has been unable to find pathological changes in that organ in cases of the kind. It is, however, quite possible that the hepatic functions may be depressed without any anatomical changes being detectable either with the naked eye or the microscope.

2. *Extirpation of the Pancreas.*—Minkowski was the first to show that removal of the pancreas in animals leads to a glycosuric condition, and this has been recognised as a true diabetes in which there is an impairment of the capacity of the cells of the body to prepare the sugar for oxidation. Many cases of diabetes in man are undoubtedly produced by disease of the pancreas. It is a long way from man to the low group of fishes called selachians (dog-fish, &c.), but even here extirpation of the pancreas causes sugar to appear in the blood;[85] there are obvious difficulties in examining the urine of such animals.

It has been generally assumed that pancreatic diabetes is not nervous in origin, since injury to the nerves in the region of pancreas and duodenum does not produce it; nor is it due to the loss of the pancreatic juice in the intestine. The usual theory adopted is that it is produced by the loss of an internal secretion, formed normally in the pancreas and distributed by the blood to the tissues, where it influences carbohydrate metabolism in some way. The little groups of epithelium cells scattered through the connective tissue of the organ, looking like a number of ductless glands in miniature and called the Islets of Langerhans, were at one time considered to be the site of the formation of the internal secretion; it has, however, been shown that the islets are only phases in the life-history of the ordinary secreting acini, and so it is difficult to accept this exclusive view.

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[85] Diamare, *Abstr.*, 1907, ii, 285. On the amount of glycogen in the livers of these fishes, and its relationship to fats, see Bottazzi, *ibid.*, 979.

Lépine's idea was that sugar destruction or glycolysis was accomplished by the pancreatic internal secretion *in the blood*, and therefore when the pancreas was removed glycolysis ceased and sugar accumulated in that fluid. This was regarded as improbable from the first, for metabolic processes do not occur in the circulating fluid any more than respiratory processes do; it has since been abundantly disproved. It may, however, still be that the active principle of the pancreatic internal secretion stimulates the glycolytic action *of the tissue cells*; and O. Cohnheim published some experiments which appeared to prove this, for he found that extracts of pancreas, added to muscles, facilitated what did not occur markedly in its absence, namely, a combustion of sugar there. Unfortunately, subsequent observers failed to obtain the same result, so that we are still in the dark as to the exact *modus operandi* of how it is that the pancreas exercises this most important rôle. During the last year, however, E. W. Hall[86] has confirmed Cohnheim's statements, and this observer states that the alcoholic extract of boiled pancreas will act similarly; the substance which acts as the co-operator in glycolysis is precipitable by phosphotungstic acid.

Bang[87] has included pancreatic diabetes among the conditions in which he has investigated the amount of liver-diastase. He finds that the amount of ferment is not much greater than in the normal condition, and therefore concludes that pancreatic diabetes is not due to an increased conversion of glycogen into sugar; glycogen formation is, in fact, either prevented or greatly lessened, and so this form of diabetes contrasts with that produced by puncture and other nervous agencies.

So far all observers are in agreement, or only manifest differences of opinion on minor points or in the explanation of the observed facts. Pflüger's recent article[88] therefore came as a bomb-shell into the physiological camp when he announced his complete dissent from everybody else. He found that in frogs extirpation of the pancreas produced fatal diabetes; that death or diabetes was not prevented by the transplantation of the pancreas from another frog into the one from which the organ had been removed; that extirpation of the duodenum or complete separation of the duodenum from the pancreas produced equally severe diabetes, even although the pancreas was not interfered with in the least, and finally that corresponding results were obtained also in dogs. His conclusion is that the internal secretion theory of pancreatic diabetes is a myth, and that the condition is produced solely by nervous disturbances.

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[86] *Abstr.*, 1907, ii, 369.

[87] *Loc. cit.*

[88] *Abstr.*, 1907, ii, 639.

Those who know Pflüger's love of polemics will, even without reading his papers, be able to imagine their style. It may be that he has discovered serious flaws in the methods of those who have obtained different results; it may be that he is right in his present conclusions; on the other hand, he may be wrong; only the future can show.

Whatever may be the result of this controversy, another has been finally settled during the year, and that is that the treatment of diabetes by secretin, recommended by Moore and his colleagues,[89] is of no avail.[90]

3. *Administration of Phloridzin.*—Many poisons produce temporary glycosuria, but the most interesting and powerful of these is phloridzin. The diabetes produced is very intense. Phloridzin is a glucoside, but the sugar passed in the urine is too great in amount to be accounted for by the small quantity of sugar in the drug; and, further, a derivative of phloridzin, which is free from sugar and called phloretin, produces the same results. It is, however, stated by Bang, Ljungdahl, and Bohm[91] that in phloridzin diabetes there is little or no increase in the liver-diastase, whereas there is an undoubted increase of this ferment in phloretin diabetes. I feel doubtful whether this can be considered to prove that the mechanism in the two cases is different.

These drugs produce diabetes in starved animals,[92] or in those in which any carbohydrate store must have been got rid of by the previous administration of the same drug. This form of diabetes is therefore analogous to those intense and serious forms of diabetes in man in which sugar is excreted in spite of abstinence from carbohydrate food, and must therefore be derived from protoplasmic metabolism. A striking feature in phloridzin diabetes is the absence of an increase of sugar in the blood; it is glycosuria without glycæmia. Moreover, if the phloridzin is directly injected into one renal artery, sugar rapidly appears in the secretion of that kidney and later in that of the other kidney. The sugar in this condition must be formed by the kidney from some substance in the blood, and it is at present unknown what that substance is. It is probably protein in nature, and most proteins contain a small amount of a carbohydrate radicle (glucosamine); but the large amount of urinary sugar is with difficulty accounted for in this way. The mucins and mucoids of the body contain the same carbohydrate substance in much greater quantity, though it is doubtful whether they participate to any great extent in general metabolism. Bywaters[93] surmises that the blood contains one of these complex proteins, which he terms sero-mucoid, but again we have the difficulty that if this is the means of sugar transport the quantity of sero-mucoid in the blood is very small.[94] It is now generally admitted that the sugar originates, not from any carbohydrate linked to the protein, but through the intermediation of certain amino-acids. The fact that the nitrogen of the urine generally rises in amount is another indication of protein breakdown. Graham Lusk[95] has made a special study of the dextrose : nitrogen ratio, and finds that in phloridzin diabetes, after all the carbohydrate store of the body has been got rid of, it is a constant one, namely, 3·65 : 1. We have here a proof that in this form of the disease the sugar has an exclusively protein origin; indeed, nearly 50 per cent. of the protein molecule must be converted into sugar. If the same ratio occurs in a man (on a diet containing no carbohydrate) or any approach to it, practitioners may be quite certain they are dealing with a serious case, and that a rapidly fatal issue in such case may be foretold with certainty has already been exemplified in Lusk's hands.

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[89] *Abstr.*, 1906, ii, 186, 787.

[90] Bainbridge and Beddard, *ibid.*, 786; N. B. Foster, *Abstr.*, 1907, ii, 189; Dakin and Ransom, *ibid.*, 189.

[91] Compare *Abstr.*, 1907, ii, 900.

[92] Pflüger (*ibid.*, 1908, ii, 52) states that hunger does not cause by any means a complete disappearance of glycogen either in dogs or frogs. In the latter animals, the amount may even increase during the winter's abstinence from food.

The amino-acid which of all others acts as the intermediary between protein and sugar is alanine. The relationship of alanine to the carbohydrates is a near one, for if the hydroxy- is substituted in its molecule for the amino-group we get lactic acid. It has been found that feeding rabbits with alanine leads to glycogen formation in their livers and to the passage of lactic acid into their urine. Another protein cleavage product, aspartic acid, acts in the same way, and this also is easily intelligible on chemical lines, for if aspartic acid loses carbon dioxide it is converted into lactic acid, and it is no great step from this to sugar.

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[93] *Abstr.*, 1907, ii, 105.

[94] Quite a number of papers have appeared during the year on the question of the state of sugar in the blood. Edie and Spence (*Abstr.*, 1907, ii, 184) state that it is present (1) in the free state, (2) in combination with protein and lecithin, (3) as a polysaccharide; according to them the corpuscles contain no sugar. Asher and Rosenfeld (*ibid.*, ii, 279) state that all the sugar, like the sodium chloride, is free. This conclusion, which is based on dialysis experiments, is criticised by Pflüger (*ibid.*, ii, 367). Lépine and Boulud (*ibid.*, ii, 562) consider it is present largely in the form of glucosides, from which it can be liberated by invertase, emulsin, &c. Embden, Lüthje, and Liefmann (*ibid.*, ii, 889) discuss the influence of external temperature on the blood sugar; cold increases, and warmth diminishes it. Cold lessens the hepatic glycogen, and the increase of blood sugar is regarded as an increased supply on its way to the muscles, the seat of combustion.

[95] *Abstr.*, 1905, ii, 187.

Glaessner and Pick[96] corroborate these views in experiments on rabbits suffering from phloridzin diabetes; the giving of alanine and glutamic acid caused most sugar to appear, leucine and glycine less, and asparagine none. They found also that if the animals were fasting no amino-acid led to any increase of sugar; obviously in the fasting animal the amino-acids given were retained and not immediately broken up. Another interesting point they made out in these experiments was that the liver of phloridzinised animals given subcutaneously to other animals produced glycosuria in the latter.

In this relation I must allude to some work by K. Grube.[97] He perfused the liver of tortoises with Ringer's solution, to which he added various sugars; galactose and lævulose produced a small and dextrose an enormous increase in the hepatic glycogen. Other sugars gave a negative result, and so also did certain amino-acids of which he used glycine, alanine, and leucine. The negative result with alanine cannot be considered a very serious objection to the views I have advanced in the preceding paragraphs, for no doubt it is explained by the fact that in the tortoise metabolism is very sluggish, although probably not different in kind from that seen in warm-blooded animals.

Acidæmia.—This question, so closely related to diabetes, is the last one I shall discuss. The words acidosis and acidæmia have almost entirely replaced the word acetonæmia in medical writings on diabetes. It has been proved that neither acetone nor its parent substance acetoacetic acid is the actual cause of diabetic coma. Both of these originate from certain fatty acids, of which the most toxic is β-hydroxybutyric acid or its amino-derivative. This undoubtedly arises from fat, from which it appears that in diabetes there is not only an inability to oxidise carbohydrate, but also to oxidise fat with the usual final products, carbon dioxide and water. In these cases the alkalinity of the blood, and also its carbon dioxide, are reduced, and the ammonia of the urine is increased. This indicates an attempt of the body to neutralise the poisonous acid. Ammonia production is the physiological remedy for increase of acids, or, to put it more correctly, less of the ammonia which results from katabolism is converted into urea. Of late years, however, pathologists have seen reason to doubt whether acidæmia is constantly present in diabetes, or even in diabetic coma; no doubt there are other factors to be considered also, and numerous papers are being continually presented on the subject; I cannot say that any of those which appeared last year throw any important new light on the subject, and the only one I shall refer to is by Allard,[98] which deals with the subject from the quantitative standpoint; systematic observations on the course of the excretion of acetone, β-hydroxybutyric acid, &c., have hitherto been lacking. Allard's estimations do not go very far, and he wisely abstains from drawing conclusions, but this is the sort of work which will have to be performed before pathologists are able to discuss logically their views on the subject.

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[96] *Abstr.*, 1907, ii, 41.

[97] *Ibid.*, 565.

4. *Administration of Adrenaline.*—This is a drug which produces so many interesting results that at least a mention of the fact that it also produces glycosuria is demanded. At present, however, but little is known of the way in which the drug causes this result. Adrenaline diabetes is one in which glycæmia accompanies the glycosuria; it largely depends on the amount of carbohydrate in the food, but, as in diabetes generally, there is an increased decomposition of protein material leading to an increase of the urinary ammonia and urea. Herter thought the drug operated through the pancreas, but Noel Paton[99] states that this is incorrect, because in birds without a pancreas (in these animals extirpation of the pancreas does not produce diabetes in itself) the drug causes glycosuria as effectively as in normal animals. Underhill and Closson[100] were unable to confirm Paton's statements respecting the effect of the drug on protein metabolism; they regard the condition as essentially nervous and consider that the poison acts on the sympathetic, so preventing carbohydrate storage or leading to a depletion of any carbohydrate store already present.

W. D. HALLIBURTON.

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[98] *Abstr.*, 1907, ii, 639.

[99] *Ibid.*, 1905, ii, 106.

[100] *Ibid.*, 1906, ii, 787.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE record of the year includes no notable discovery nor any paper that is likely to be reckoned in the future as of fundamental importance; in several directions, however, good progress has been made, although, as the subject opens up, it is only to disclose its increasing complexity. Agricultural chemistry is essentially a border-line science, dwelling on the confines of chemistry and physics, botany, and physiology alike, touching these subjects also just where they are most difficult and obscure. The chemistry of the growing plant and of the feeding animal is the chemistry of the proteins and the carbohydrates, of enzyme action, and of the varied functions of the cell, whilst the study of the soil at once leads to some of the most difficult problems of solution, and of the interaction of molecular and chemical forces which take place in the thin films surrounding the soil particles.

Soil Bacteriology.

Considering first the soil, the part played by the organisms contained therein assumes every year a greater importance; it becomes increasingly evident that plant production in the open field, and the effect of fertilisers and even of cultivation, are determined by the nature of the soil flora and the repression or encouragement of particular groups of micro-organisms. The free organisms in the soil that can fix atmospheric nitrogen continue to receive considerable attention, and the chief conditions of their activity—a supply of oxidisable carbohydrate, from which they may derive the necessary energy, and the presence of calcium carbonate to neutralise the acids produced—may be regarded as established; it is the magnitude of the part played by *Azotobacter* and its congeners, under natural conditions, that remains to be determined. A. Koch and his colleagues at Göttingen[1] show that the addition of dextrose, sucrose, soluble starch, or straw to soil brings about an increase in the amount of nitrogen it contains;

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[1] *Abstr.*, 1908, ii, 56.

the best effect was obtained by a single application of 2 per cent. of dextrose, when 8 to 10 milligrams of nitrogen were fixed for each gram of sugar added. They also showed that the nitrogen compounds formed by the *Azotobacter*, the chief organism concerned, were easily nitrified; as a consequence, when sugar was added to soil in pots in which successive crops of oats and buckwheat or sugar beet were grown, the nitrogen fixation induced by the sugar became evident in an increased yield. The first crop of oats was reduced, the unchanged sugar acting injuriously on the growing plant, but in the following year the yield of buckwheat or beet was much increased, being nearly trebled where 4 per cent. of sugar had been added. At the end of the experiment, the sugar-treated soil was also found to have been enriched in nitrogen. That the depression of the first crop was due to the injurious effect of the unaltered sugar was shown by another experiment, in which the soil, after the addition of the sugar solution, was kept in an incubator for four weeks. Oats were then sown, which yielded more than double the amount of dry matter that was obtained in the check experiments, where the soil received no sugar. These experiments constitute the first direct experimental demonstration that *Azotobacter* can play a practical part in provision of nutriment for the higher plants.

H. R. Christensen[2] has dealt with the importance of calcium carbonate and the phosphates in the nutrition of *Azotobacter*. He showed that the occurrence of *Azotobacter* in various soils stands in close relationship to the amount of calcium carbonate in the soil, exceptionally active soils always possessing an alkaline reaction, which confirms the observations of S. F. Ashby on the Rothamsted soils.[3] He even considers that the growth of *Azotobacter* will form the most trustworthy evidence that can be obtained of the presence of traces of calcium carbonate in soils. J. F. Lipman[4] also used *Azotobacter* as a test of the state of the mineral constituents of the soil, and reaches much the same conclusions as Christensen, whilst Wilfarth and Wimmer[5] found the presence of phosphoric acid essential.

As regards fixation of nitrogen by the nodule organisms of the leguminosæ, no new step can be reported; various preparations of the organism are being widely used[6] in a practical way for the inoculation of seed or soil before a leguminous crop, although the best way of preserving the cultures in an active condition has

[2] *Centr. Bakt. Par.*, 1907, II, **17**, 109, 161, 378, 735.

[3] *J. Agric. Sci.*, 1907, **2**, 35.

[4] *Report New Jersey Agric. Exp. Station*, 1907.

[5] *Abstr.*, 1907, ii, 809.

[6] See Remy, *Centr. Bakt. Par.*, 1907, II, **17**, 661.

not yet been settled.[7] But, although inoculations may be of the greatest possible benefit in introducing the appropriate organism into soils which have never previously carried the leguminous crop in question, such soils are exceptional, and it is not yet demonstrated that there is any return for the inoculation of ordinary cultivated land. It is uncertain whether more active races of the clover organism, for example, can be distinguished, and, further, it is uncertain if such improved races, when introduced into ordinary soil swarming with kindred organisms, can survive the competition that results, so as to produce any permanent effect upon the crop.

As regards nitrification, perhaps the most important of the bacterial processes in the soil, Kaserer[8] reports the isolation of another bacterium, *B. nitrator*, which forms nitrates from ammonia in a single operation. Hitherto, no nitrifying organisms have been detected other than those first distinguished by Warington and then isolated and described by Winogradsky, *Nitrosmonas* and *Nitroscoccus*, which oxidise ammonia to nitrite, and the *Nitrobacter*, which completes the change to nitrate. Müntz and Lainé[9] have been studying the nitrification process on a large scale to ascertain if the old nitre beds could be so far improved as to become practical sources of nitrate, supposing the conditions of a century ago were to recur and France were again cut off from any external supply of Chilian or Indian nitrate. Müntz obtained the most intensive nitrification when a weak solution of ammonium sulphate percolated through a layer of some medium offering a large surface, peat proving the most effective when an excess of calcium carbonate was maintained. The inhibiting effect of organic matter on nitrification does not hold for the humic compounds of peat. A strong solution of ammonium sulphate cannot be nitrified, but by repeatedly adding further small amounts to a solution that has already been oxidised, and passing it again through a nitrifying bed, the concentration of the calcium nitrate could at last be raised to about 4½ per cent. Some little time was necessary before the beds reached this efficiency, since the nitrifying organisms only gradually become habituated to working in solutions of such a concentration. In view of the rapid development of the electrical processes for making nitrates, it is improbable that Müntz's improved nitre beds will ever be required.

Perhaps the most interesting question in soil bacteriology which has of late been opened up, is concerned with the increased productiveness shown by soil that has been subjected to some process of partial sterilisation, such as heating to the temperature of boiling water, or treatment with volatile antiseptics like carbon disulphide or toluene. The facts have been disclosed in a more or less accidental fashion by various workers during the last ten years or so, but it is only just lately that they have attracted much attention, or have been seen to possess any general significance. Various papers on the subject appeared during 1907 (Heinze,[10] Koch[11]), including one by F. V. Darbishire and E. J. Russell,[12] which traverses the whole ground very thoroughly. In continuance of the work of these authors on the rate of oxidation in soils,[13] they were led to observe that soils which had been heated to 100°, or treated for a time with volatile antiseptics, always showed a higher rate of oxidation than the same soils untreated. As they had previously established an interdependence between the rate of oxidation and the fertility of a soil, they proceeded to test the effect of such treatment upon the productiveness of soils by means of experiments in pots. The soils were either heated for two or three hours to a temperature of 90—95°, or treated in their pots for about a week with a small quantity of carbon disulphide, toluene, or chloroform, after which they were spread out in thin layers until all trace of the antiseptic had volatilised; no trace of the antiseptic could be detected by any of the tests then applied. Various crops were grown in the pots, and in all cases the treated soil yielded a greater weight of dry matter than the untreated soil, the increase being generally from 10 to 40 per cent., but occasionally as high as 70 to 90 per cent. The beneficial effect of the treatment was also seen when a second crop was taken without further disturbance of the soil, but it did not extend to the third crop. Not only was the dry matter increased, but it was, as a rule, richer in nitrogen, phosphoric acid, and potash, so that the crop always removed larger amounts of these fundamental nutrients from the treated soil.

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[7] R. G. Smith, *Abstr.*, 1907, ii, 498.

[8] *Ibid.*, 381.

[9] *Bull. Soc. d'encouragement pour l'Industrie Nationale*, 1907, **109**, 951.

The result of heating the soil was even more marked; except in the case of certain leguminous plants, the yield of the heated soil was generally doubled or even trebled, and again the effect persisted to the second, and sometimes to further crops.

It is impossible to explain these results from a purely chemical point of view, for, even if the heating might be supposed to render more available the store of plant food in the soil, no corresponding action could be attributed to the vapour of toluene or chloroform. It was demonstrated that the soils were not completely sterilised by the treatment, and the most tenable explanation is that the partial sterilisation exercises some selective action on the groups of bacteria in the soil, destroying some which are unfavourable to the growth of the plant, and thereby giving other beneficial forms, like the oxidising bacteria, a greater scope. One of Darbishire and Russell's experiments is rather significant in this connexion; they found that if they watered the heated soil with ordinary well-water, it lost some of its superiority over the untreated soil, thus indicating that the beneficial rearrangement of the original soil flora brought about by the partial sterilisation can only persist when the soil is watered with sterile water introducing no new forms.

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[10] *Abstr.*, 1907, ii, 388, 502, 572.

[11] *Ibid.*, 647.

[12] *J. Agric. Sci.*, 1907, **2**, 305.

[13] *Ann. Report*, 1905, 251.

With this work of Darbishire and Russell's may be connected an investigation by O. Rahn[14] on the effect that drying soil at the ordinary temperature has on its bacteriological properties. Soil which had merely been allowed to dry was found to induce greater bacteriological changes, as, for example, production of acid in dextrose solutions, production of carbon dioxide in sugar solution containing calcium carbonate, formation of ammonia in urea or peptone solutions, than did the same soil after storage in a moist condition. These effects were most manifest with a rich garden soil, but it was not settled whether they were to be regarded as accelerations due to drying, or depressions brought about by storage in a moist state. The number of the bacteria (growing upon gelatine) in the soil was always diminished by drying, and the author considers that his results show the effects were due to some substance formed in the soil by drying, which is soluble, not decomposed by boiling its solution, and not of the nature of an ordinary plant nutrient. Experiments on the effect of a preliminary drying of the soil on mustard in pots were not conclusive.

The susceptibility of the soil to changes of this kind is a question still open to a good deal of elucidation, but it already promises results which may attain considerable practical importance; meantime, it also serves to emphasise the necessity for caution in drawing conclusions from any experiments on soil, when what is apparently so small a disturbance can bring about such a radical change in its productiveness.

Soil Chemistry.

In this section of our subject there is nothing novel to report, although Whitney and his colleagues of the Division of Soils (U.S. Department of Agriculture) have issued several bulletins,[15] in which they continue to develop their somewhat remarkable theory of the functions of soil and fertilisers, a theory which has

[14] *Centr. Bakt. Par.*, 1907, II, **20**, 38.

[15] See particularly Bulletins Nos, 36, 40, and 47.

found no acceptance, nor much consideration, among European chemists.[16]

Briefly, Whitney's theory is that soils become infertile through the accumulation of toxic substances excreted by the roots of crops, and that fertilisers act, not by directly feeding the plant, but by in some way destroying or putting out of action these toxic excretions. The experiments brought forward in support of this theory are chiefly made with wheat seedlings in water cultures, the seedlings being from six to twenty days old, and therefore still drawing their nutriment from the endosperm. The reports go to show that the growth of such seedlings in distilled water is injured by the addition of an aqueous extract of certain soils, but that the injurious effect of the extract can be removed by a preliminary filtration through finely-divided carbon, shaking up with ferric hydroxide or calcium carbonate, and, as a rule, by boiling. Other experiments showed that water in which such seedlings have been grown for a time acts injuriously on the growth of a new batch of seedlings, but that filtration through carbon, &c., as before, restores the water in which the seedlings have been grown to a normal condition suitable for renewed growth. Distilled water containing very small amounts of such plant products as neurine, guanidine, coumarin was also shown to be hurtful to the development of the seedlings, but was again improved by the treatment described before. Many questions suggest themselves in reading these interesting reports and the speculations they give rise to, but criticism is as yet impossible; the data supplied afford no means of estimating the magnitude of the experimental error, which is known to be great in experiments of this kind, and the experiments themselves are never pushed to the point of becoming really critical of the theory, the authors seeming to be content to multiply results "which may be explained by supposing," or are "in accord with the assumption upon which the experiment was made." Here, in Europe, we must suspend our judgment until we receive a more critical version of the work.

The perennial question of the most suitable solvent to use for the determination of the "available" mineral plant food in the soil continues to receive attention. E. A. Mitscherlich[17] selected water saturated with carbon dioxide, which substance he regards as the main secretion of the plant's roots, and the effective solvent under ordinary soil conditions (see also Stoklasa, &c.[18]). He then proceeded systematically to the examination of one or two soils with the view of determining the effect of the concentration of the carbon dioxide in the solution, of the duration of the action, and of temperature, so as to arrive at the probable error attaching to estimations of this method. It is noteworthy that the temperature factor is considerable for the potash and nitrogen, but not for phosphoric acid or lime, although it has hitherto been neglected in considering these various methods of extraction of weak solvents. No attempt was made by Mitscherlich to correlate his results with the behaviour of the soils in the field; this, however, was the prime object of A. de Sigmond,[19] who has examined Hungarian soils by an entirely different method. de Sigmond started from some experiments of Schloesing's,[20] who showed that if a series of samples of soil be attacked by very dilute solutions of nitric acid, the strength of which increases by steps, the amount of phosphoric acid dissolved increases at first with the strength of the nitric acid solution, then remains constant for a time, and then begins to rise again. This second increase, according to Schloesing, marks the point at which the nitric acid becomes more than strong enough to dissolve all the "available" phosphoric acid, so that it then begins to attack the more insoluble compounds present in the soil. de Sigmond generally discusses the results obtained by this method, which was thus tried for the first time on a large scale, and obtained a considerable agreement between them and the behaviour of the soils towards phosphatic fertilisers, as judged by a series of field and pot experiments, which are also reported.

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[16] See, however, Pouget and Chouchak, *Compt. rend.*, 1907, **145**, 1200.

[17] *Landw. Jahrbucher*, 1907, **36**, 309.

[18] *Abstr.*, 1907, ii, 717.

Another question which dates back to the earliest days of agricultural chemistry, the withdrawal of ammonia from its compounds, and its retention by the soil, has been re-examined during the year by A. D. Hall and C. T. Gimingham.[21] These authors found that the action was always one of double decomposition, either with the zeolitic double silicates of the soil, ammonium being withdrawn and an equivalent amount of calcium, magnesium, potassium, or sodium taking its place in the solution, or with humus (calcium humate), in which case an equivalent amount of calcium again replaced ammonium in the solution. No measurable amount of adsorption of the salt, as a whole, or of selective absorption of the base, so as to leave the solution acid, was observed, even when the solutions were evaporated at the ordinary temperature in a current of air, or exposed to the action of a stream of carbon dioxide. The authors give an empirical formula connecting the amount of change with the concentration of the ammonium salts in the solution when the amount of clay in equilibrium with the solution is in excess, but do not establish any theoretical justification for the formula arrived at. The authors also considered the interaction of ammonium salts and calcium carbonate, but showed that the presence of this constituent affects but little the removal of ammonia from solution by the clay and humus. They therefore regard the retention of ammoniacal fertilisers by the soil as due to clay and humus without the preliminary reaction with calcium carbonate that is sometimes regarded as necessary.

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[19] *Abstr.*, 1907, ii, 717.

[20] *Ibid.*, 1899, ii, 449.

[21] *Trans.*, 1907, **91**, 877.

R. A. Robertson, Irvine, and Miss Dobson [22] have begun a fresh study of humic acid, which they have extracted from peat, and also prepared by the action of hydrochloric acid on sugar. The elementary composition of the two products were compared, and, besides differences in the percentage of carbon, the natural acid always contained nitrogen, and probably iron. It yielded fewer methoxyl groups than did the artificial acid, and, when compared as a source of carbon for the growth of *Penicillium*, the artificial acid was better than the natural, but inferior to glucose. S. Suzuki [23] has also examined natural humic acid by hydrolysing it with strong hydrochloric acid; from the products, he isolated alanine, leucine, aspartic acid, and small quantities of proline and other amino-acids.

Several reports on the analysis, chemical and mechanical, of a series of English soils have been published during the year, and, as the analyses have been carried out on a uniform system, there is steadily being accumulated a mass of data for a general chemical survey of the soils of our country.

C. M. Luxmoore [24] described the composition, mechanical and chemical, of one hundred samples of soil and subsoil from Dorsetshire, the soils being derived from each of the tertiary and secondary formations between the Bagshot Beds and the Lower Lias; F. W. Foreman [25] dealt with soils from Cambridgeshire, generally derived from the same formations as those discussed by Luxmoore, and S. F. Armstrong [26] attempted to correlate the composition of a number of meadows and pastures in the eastern counties with the chemical and botanical composition of the herbage.

Soil Physics.

The physics of the soil is, perhaps, at the present time the most neglected branch of agricultural science, yet it ought to be very attractive to any investigator, if it were only for the bearing it has on the practical operations of cultivation and management of the soil, which are of such prime interest to the working farmer.

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[22] *Abstr.*, 1907, i, 894.

[23] *Bull. Coll. Agr. Tōkyō*, 1907, **7**, 513. See also A. J. van Schermbeck, *Abstr.*, 1907, ii, 648.

[24] *Report*, Reading University College.

[25] *J. Agric. Sci.*, 1907, **2**, 161.

[26] *Ibid.*, 283.

During the past year few papers bearing on this subject have appeared, nor has any new line of inquiry been opened up. Von Seelhorst and his colleagues at Göttingen[27] have continued their studies of the effects of variation in the water content and temperature of the soil on the composition and yield of various crops, the experiments in this case being made on oats and spring wheat.

R. S. Vinson and E. J. Russell[28] gave an interesting series of temperature readings to illustrate the well-known fact that the bottoms of valleys are colder than the slopes on either side. The results agree with the usual explanation that the cooled air flows down the sides and accumulates in the bottom of the valley, but they also indicate that the actual river bank is warmer than land a little further back from the water, the rise in temperature being particularly marked on any piece of land more or less surrounded by water.

Another perennial problem, the flocculation or coagulation by means of salts of turbid liquids, such as suspensions of clay in water, has again been dealt with by A. D. Hall and G. G. T. Morison.[29] These authors have endeavoured to obtain quantitative measurements by using a constant amount of a graded kaolin diffused in a constant volume of water. The effect of various salts, &c., on jars filled with such a turbid medium were estimated by matching them against a standard series in which the flocculation was brought about by regularly increasing amounts of calcium nitrate. The authors show that the amount of material flocculated was proportional to the amount of flocculating salt added up to a certain point, above which any increase of salt produced no further effect; there was no adsorption of the salt, nor did flocculation involve any growth or permanent aggregation of the fine particles of the suspended matter. Conductivity measurements, while flocculation is going on, indicated that no perceptible change occurred in the amount of salts in solution. The acids were the most effective flocculators, and aluminium salts were almost equally effective. Calcium and barium were less than half as effective, magnesium came a little below calcium, potassium had only about one-fifth the value of calcium, and sodium only about half that of potassium, equivalent for equivalent. The nature of the acid radicle had an influence on the flocculating power of the salt, the order being hydrochloric, nitric, sulphuric, acetic (the chloroacetic acids had the same value as acetic acid itself); the same comparative order held for the salts as for the free acids. Oxalic and tartaric acids were feeble flocculators; citric acid, glycine, or

[27] *J. Landw.*, 1907, **55**, 233.

[28] *J. Agric. Sci.*, 1907, **2**, 221.

[29] *Ibid.*, 244.

phenol were without action. Soluble hydroxides such as caustic soda, potash, or ammonia opposed flocculation; calcium and barium hydroxides gave, however, positive effects, but much below those shown by their other salts, the flocculating effect of lime in practice being due to the formation of calcium bicarbonate, which is a very effective salt. Many substances, for example, bauxite and hydrated ferric oxide, do not form true suspensions in water, which property the authors regard as conditioned by the presence of double silicates, which hydrolyse and yield a little soluble alkali on contact with water. On this theory, flocculation is brought about by the neutralisation or throwing back into combination of the free alkali, although any final clearing up of the subject must be preceded by an explanation of the Brownian motion, which characterises particles in true suspension in a turbid liquid.

Chemistry of the Growing Plant.

1. *Nutrition.*—Although nothing very striking is to be reported in connexion with the nutrition of the plant, Fenton's synthesis of formaldehyde[30] from carbon dioxide by reduction of the aqueous solution with magnesium should be noted as the first reduction of carbon dioxide that has been accomplished at the ordinary temperature. This may be regarded as a step forward, although the synthesis is not of a type which can be imagined as taking place within a plant's cell; still, the evidence seems to be increasing that formaldehyde forms one of the steps in the natural process of photo-synthesis. G. Kimpflin[31] detected formaldehyde in the leaf of *Agave* by injecting a solution of sodium hydrogen sulphite containing *p*-methylamino-*m*-cresol, which forms a red precipitate with formaldehyde, but not with other aldehydic compounds.

Although the function of the various mineral constituents of the plant is very far from settled as yet, a number of contributions to the subject have been made during the year. H. S. Reed[32] has eliminated some of the difficulties inherent in the problem by working with algæ like *Spirogyra* in water cultures, from which the potash, the phosphoric acid, or other constituent in question could be omitted as desired. In this way, he observed that, in the absence of potash, all starch formation was suspended, and the granules originally present in the cells gradually disintegrated and disappeared. The lack of phosphoric acid proved very injurious, especially to the reproduction of the cells; there was no mitotic division of the nucleus, and there was an abnormal formation of cellulose.

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[30] *Trans.*, 1907, **91**, 687.

[31] *Abstr.*, 1907, ii, 289.

[32] *Ann. of Botany*, 1907, **21**, 501.

In the absence of calcium salts, new cell walls were imperfectly formed, and the production of cellulose ceased, whilst magnesium appeared to be essential to the activity of the chloroplasts, since in its absence no oil globules were to be found, and the chlorophyll assumed a yellow colour. The latter observation is interesting in connexion with the important work by R. Willstätter[33] and his colleagues on chlorophyll and its derivatives, which they have shown to be compounds of magnesium, without any iron.

D. Lienau and A. Stutzer,[34] experimenting with oats, found that phosphoric acid promotes thickening of the cell walls, which, however, was diminished by potash and nitrogen. In consequence, phosphoric acid most promoted the stiffness of the straw. These results, as regards potash, are hardly in accord with former observations, or with the known function of potash to promote carbohydrate formation.

The long-debated question of whether the roots of plants secrete an acid, which aids in the nutrition of the plant by effecting the solution of the mineral constituents of the soil, has been the subject of further investigation. Kunze[35] reviews the evidence again, and concludes that only carbon dioxide is excreted. He does not, however, regard this as capable of bringing enough material into solution, and shows that the acid excretion from the mycelium of fungi in the soil is more effective.

Schreiner[36] brings evidence to show that the roots of seedlings both excrete acids and possess oxidising powers, but no argument as to plant roots generally can be drawn from the behaviour of the roots of autotrophic seedlings. Stoklasa and Ernest[37] also regard carbon dioxide as the effective natural solvent of minerals in the soil, and have been continuing their investigations on the amount that is excreted by plant roots and by micro-organisms in the soil. Under natural conditions, they obtain 15 milligrams of carbon dioxide in twenty-four hours from a kilogram of the soil they worked with.

Work continues to be reported on that much-debated question, the stimulus to plant production brought about by minute traces of metallic salts and other substances which in higher concentrations act as poisons. Despite the numerous investigations on the subject, for example, by Raulin, by Loew and his pupils in Japan,[38] by J. A. Voelcker in this country,[39] the prime fact of stimulus by minute traces of poison cannot be regarded as established. Increased growth has, doubtless, been observed to follow the application of such substances to the soil, but, as may be seen from the effects of antiseptics, previously reported, the soil is excessively complex and its equilibrium is easily disturbed. Hence it is by no means safe to conclude that any increased growth following the application of a manganese salt, for example, is due to the stimulus of the manganese to the plant. Kayser and Marchand [40] have studied the effect of small additions of manganese salts to alcoholic fermentations. They find that the start of the fermentation is sometimes checked by the presence of manganese, but that eventually higher proportions of alcohol, glycerol, and acids are produced from a given weight of sugar. Yeasts that have been habituated to comparatively strong solutions of manganese salts by growing in solutions of gradually increasing strength become particularly active, and will both induce a more rapid fermentation and push it further, especially if a small quantity of manganese salt is present in the fermenting liquid. Bertrand [41] applied manganese sulphate at the rate of 50 kilos. per hectare to land on which wheat was sown, and obtained an increase in the total crop of 22·5 per cent., the corn being raised 17·4 per cent., and the straw 26 per cent. Here, again, there is no means of deciding whether the application of any other soluble sulphate might not have been equally effective by bringing into solution some of the dormant bases of the soil. G. Salomone [42] and S. Uchiyama [43] report very similar results, in which even manganese dioxide exerted a beneficial influence on crops in the open field. A. Amos [44] attacked the problem from a different point of view. Various preparations of copper (of which the most widely used is Bordeaux mixture, prepared by precipitating copper sulphate solution with lime [45]) are sprayed on the leaves and act as fungicides, but they are also credited with bringing about a longer life of the leaf, and an increase of crop, when no fungoid disease attacks the plants. Flowers of sulphur are dusted on to leaves for the same purpose. To ascertain if these substances acted as stimulants to the processes carried on by the leaf, Amos compared the rates of assimilation of two leaves upon the same plant before and after one of them had been treated with the fungicide, using Brown and Escombe's apparatus for the measurement of the rate of assimilation. The only result of the treatment with the fungicide was such a falling off in the rate of assimilation as might be expected from the inevitable blocking of the stomata, nor was any indication obtained that the activity of the leaf was

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[33] *Abstr.*, 1907, i, 69, 71, 784.

[34] *Ibid.*, ii, 47.

[35] *Jahrb. für. Wiss. Bot.*, 1906, 357.

[36] *Abstr.*, 1907, ii, 715.

[37] *Zeitsch. Zuckerind. Böhm.*, 1907, **31**, 291.

[38] *Ann. Report*, 1906, 257.

[39] *Ibid.*

[40] *Abstr.*, 1907, ii, 288, 383, 903.

[41] *J. d'Agric. Pratique*, 1906, 42.

[42] *Abstr.*, 1907, ii, 982; also W. van Dam, *ibid.*, 649.

[43] *Bull. Cent. Exp. Sta. Japan*, 1907, **1**, 37.

[44] *J. Agric. Sci.*, 1907, **2**, 257.

[45] Pickering, *Trans.*, 1907, **91**, 1988.

maintained to a greater age as a consequence of the treatment. The experiments were made with the leaves of the vine, and hop, and the artichoke (*Helianthus tuberosus*), for which plants values of the rate of assimilation had not previously been obtained.

2. *Plant Constituents and Changes of Composition during Growth.*—During the year, T. B. Wood has made an important step towards the resolution of a problem, the cause of "strength" in wheat flour, which has long occupied the attention of agricultural chemists in all countries. The question was the subject of a full debate at one of the meetings of the Chemistry Section of the British Association, and Wood's papers are published in the Journal of Agricultural Science.[46] Wood considers that strength, defined as the capacity of making large, well-piled loaves, is the outcome of two factors, one determining the size, and the other the shape of the loaf. The size is determined by the amount of carbon dioxide evolved in the dough, and this depends on the amount of sugar contained in the flour, together with that produced by diastatic action while the dough is rising. The shape of the loaf is determined by the consistency of the gluten, which does not depend on its composition, but on the salt content and acidity of the medium with which it is in equilibrium. Wood found that the gliadin and glutenin, of which gluten is made up, possessed the same composition (as far as might be judged from the products of hydrolysis), whether they were derived from strong or weak flours. By suspending pieces of washed gluten in a series of solutions in which both the acidity and the salt content varied by regular increments, Wood observed that for certain concentrations the gluten was tough and stable, while for others it disintegrated and lost all coherence. When the observations were all plotted with the salt concentrations as ordinates and acid concentrations as abscissæ, a closed curve could be drawn, all points within which represented solutions in equilibrium with the non-coherent gluten. Gluten, however, in contact with solutions represented by points outside the curve remained tough and elastic. Wood has discovered various relationships between the effect of different acids and salts known or likely to occur in flour, but the precise application of the facts to the discrimination of strong from weak flours remains to be worked out, a method for doing which is indicated. Little is known as yet of the nature or amount of the acids and salts present in an aqueous extract of flour, but these experiments show that they must exert a marked effect on the consistency of the gluten, so that in their variations a clue may be found to the abnormal behaviour of many flours. Wood also shows

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[46] *J. Agric. Soc.*, 1907, **2**, 139, 267.

that the consistency of other proteins, for example, the curd of milk, is similarly determined by the acidity and salt content of the solution with which it is in contact, and suggests that in this fact we have a general clue to the control of all such technical processes depending upon the physical properties of colloids.

Thatcher and Watkins[47] have studied the distribution of nitrogen in the different grains from the same ear of wheat, and again in different ears of the same variety. Their work goes to show that the variations thus found among the different ears of the same variety and between the grains of the same ear are due to nutrition, and are not hereditary. This result adds another to the arguments against the possibility of improving plants like wheat by "selection" alone.

Several facts of considerable chemical interest in connexion with the membranes forming the coats of seeds have been published during the year. In the first place, A. J. Brown[48] has shown that the barley grain possesses a true semipermeable membrane, through which water will pass freely, but not any of the salts which may be dissolved in the water. If, for example, unbroken barley grain is immersed in normal (4·9 per cent.) sulphuric acid, water only passed through the membrane into the endosperm, until the sulphuric acid solution outside became concentrated up to 7·6 per cent. The grain also absorbed water from 18 per cent. sulphuric acid, but failed to do so from a solution containing 36 per cent. of acid. The effective membrane appeared to be located in the spermoderm, since this layer resisted the action of 36 per cent. sulphuric acid, by which the outer layer of cells forming the pericarp was disintegrated. Iodine was the only dissolved substance that was found capable of passing through the membrane, and it seems significant that the substance so doing should also be one combining with the starch of the endosperm.

C. Bergtheil and D. L. Day[49] showed that the irregular and slow germination of the seeds of Java Indigo (*Indigofera arrecta*) was due to the preponderance of "hard" seeds, formed only when the seed crop was allowed to become thoroughly ripe. These hard seeds are practically impermeable to water, owing to a thin outer covering, neither true cellulose nor true cuticle, which can be removed by scratching or by steeping the seed for half an hour in concentrated sulphuric acid, followed by immersion in water.

Similar "hard" seeds in clovers and other European leguminous plants have been studied by Hiltner and Kinzel,[50] who recommend treatment of the seed with hot water or sulphuric acid in order to promote germination.

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[47] *Abstr.*, 1907, ii, 983.

[48] *Ann. of Botany*, 1907, **21**, 79.

[49] *Ibid.*, 57.

[50] *Zeitsch. für Landw. u. Forst. Wirts.*, 1906, 36.

Amongst other papers dealing with plant constituents, one should be noticed by E. Schulze,[51] in which he maintains that the darkening of beet and other plant juices is not due to the enzymic oxidation of tyrosine, as is commonly supposed. The tyrosine he could obtain from the juice of beet, potato, and dahlia tubers was too small in amount to account for the darkening; moreover, after darkening, the tyrosine was still there, and no trace of homogentisic acid could be detected.

In the chemistry of enzyme actions, we owe to F. Ehrlich [52] the interesting observation that fusel oil in alcoholic fermentation is derived from leucine. The leucine is split up by the enzymes, and the nitrogen-containing groups are used for the formation of proteins in the yeast cells. Ordinary leucine yields inactive amyl alcohol; *iso*leucine gives *l*-amyl alcohol.

Manures and Manuring.

As regards fertilisers, the year has nothing new to show; both field and pot experiments continue to be made with the two new products containing nitrogen derived from the atmosphere, crude calcium nitrate and calcium cyanamide,[53] and agree with previous trials to show that the nitrogen of both substances is in a highly available condition. But neither product is yet on the market on any large scale, although the small factory at Notodden is continually turning out calcium nitrate, and the Italian Cyanamide Co. at Piano d'Orta are rapidly increasing their output. It is understood that very large works are being erected for both processes, so that next season may see these fertilisers on the ordinary market.

Meantime, the two substances with which the new fertilisers will mainly enter into competition, ammonium sulphate and sodium nitrate, continue to receive considerable attention; there has been quite a revival of investigations into the relative value and actions on different soils of these two old-standing manures,[54] although it cannot be said that any new point of view has been disclosed.

Turning from the most recent to the oldest of fertilisers, farmyard manure, Schneidewind,[55] at Lauchstadt, has been continuing the very interesting series of researches begun by Maercker on the losses of nitrogen that are experienced in making dung and the best methods of conservation that can be adopted in practice. These investigations have the great advantage of being made on a large scale and under working conditions, and are not open to the objections which attach to most of the laboratory experiments that have been reported on materials for conserving dung. Schneidewind pronounces against gypsum and other materials of like nature; not only are uneconomical quantities necessary to be effective in saving nitrogen, but the calcium sulphate becomes reduced to sulphide, which afterwards acts injuriously in the soil. Instead, he confirmed his former observation that the greatest saving of nitrogen is effected if the base of each new dung-heap is made of a layer from an old fermenting heap. Schneidewind has hardly arrived at an explanation, but he thinks the difference may be brought about by the carbon dioxide evolved from the initial layer; of the experimental fact he has no longer any doubt.

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[51] *Abstr.*, 1907, ii, 293.

[52] *Ibid.*, 383.

[53] *Ibid.*, 48, 295, 573, 646, 807.

[54] H. Süchting, *ibid.*, 646; Schneidewind, *Landw. Jahr.*, 1907, **36**, 598; Kretschmer, &c., *Abstr.*, 1907, ii, 809.

[55] *Landw. Jahr.*, 1906, **36**, 569.

The losses of nitrogen in making farmyard manure have also been studied by T. B. Wood[56] in the course of a feeding experiment, in which four heifers received known weights of food, which was analysed from time to time. The dung was not disturbed, but was analysed by cutting out sections at the end of the feeding period, and again six months later. About 15 per cent. of the nitrogen in the food and litter was lost in making the dung, and on storage the loss increased to 28 per cent. for poor dung made from roots and hay only, and to 40 per cent. for the richer dung obtained by feeding also with cotton cake. Since the digestible nitrogen in such rich foods is excreted as urea, which readily ferments and undergoes loss, even under good management, it is not always possible to recover in the manure the half of the nitrogen contained in purchased foods, which is the basis now usually adopted for compensation to the outgoing tenant for the fertility he leaves behind on the farm through the feeding-stuffs he has bought and consumed during the last year of his tenancy.

Chemistry of Animal Nutrition.

A paper which is likely to have a considerable bearing on the theory of animal nutrition, since it throws light on the fact well known to practical graziers that the proteins of different foods have not the same values for putting on flesh, has been published by Miss Willcock and F. G. Hopkins.[57] They showed that when zein is the only nitrogenous food given to young mice, they soon die, but when tryptophan, which is absent from zein, is added, the survival of the animals is greatly prolonged, indicating that the

[56] *J. Agric. Sci.*, 1907, **2**, 207.

[57] *Abstr.*, 1907, ii, 109.

tryptophan group is necessary in building up the proteins specific to mice, and that it cannot be replaced by similar amino-acids like tyrosine.

The view, now generally accepted, that in digestion the proteins are broken down very thoroughly into simple amino-acids and kindred bodies, which are put through a building-up process in the intestinal wall[58] before they reach the blood, has continued to receive much discussion. It is well illustrated in an investigation of Abderhalden and his colleagues,[59] who found that feeding a dog on gliadin (a protein very rich in glutamic acid) did not increase to any marked degree the amount of glutamic acid in the blood proteins. Bound up with this subject is the question of the utilisation by animals of the non-protein nitrogenous materials in feeding-stuffs. O. Kellner[60] maintained that they can, to a certain extent, replace proteins in the diet, because they become built up into proteins by bacteria in the intestine of herbivorous animals; M. Müller[61] finds that soluble non-proteins from hay can be utilised in the formation of flesh of a dog, whilst K. Friedländer[62] found that the non-proteins of molasses fed in conjunction with food deficient in nitrogen were unable to prevent loss of nitrogen in the animal, although most of the nitrogenous compounds in the molasses could be converted by bacteria into proteins.

The parallel question of how far animal fat in the body or in the milk is reconstructed from the fat in the food is discussed in a paper by von Knierim and Buschmann.[63] Feeding milch cows with various oil-cakes, they found that both the milk yield and the composition of the butter fat, as measured by its physical properties, were affected by the feeding in a way which could only be explained by assuming that some of the fat of the food had passed into the milk unchanged. How far the fat had been broken down in digestion and then built up again was not discovered.

Analytical.

The determination of phosphoric acid continues to attract a good deal of attention; in most countries, the accepted method is to precipitate as phosphomolybdate, which is dissolved in ammonia, the phosphoric acid being reprecipitated with magnesia mixture. Since it is a lengthy and comparatively expensive process, many alternatives have been suggested, and two long and critical papers have appeared in 1907 by Mach[64] and Wagner, Kunze, and Simmermacher,[65] showing that equally accurate results can be obtained by direct precipitation with magnesia mixture in the presence of citric acid, if the silica be first removed. A critical paper on the estimation of potash as perchlorate, as applied to agricultural analyses, has been published by Schenke and Krüger,[66] who show that sulphuric, phosphoric, and hydrochloric acids must first be removed.

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[58] *Abstr.*, 1907, ii, 893.
[59] *Ibid.*, 487.
[60] *Ibid.*, 491, 794.
[61] *Ibid.*, 645.
[62] *Ibid.*, 895.
[63] *Landw. Jahr.*, 1907, **36**, 185.
[64] *Abstr.*, 1907, ii, 395.

A. D. HALL.

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[65] *Abstr.*, 1907, ii, 577.

[66] *Ibid.*, 910.

MINERALOGICAL CHEMISTRY.

PROGRESS in this branch of our science during the past year has resulted rather from steadily pushing on along old lines of inquiry than from breaking new ground, and we may at once proceed to record the advances made under the headings employed in the previous volumes of this Report.

General and Physical Chemistry of Minerals.

Salt Deposits.—The great work of van't Hoff[1] has now attained its jubilee with the appearance of the fiftieth part of the "Researches on the Formation of Oceanic Salt Deposits." This paper describes unsuccessful attempts to prepare franklandite, $Na_2CaB_6O_{11},7\frac{1}{2}H_2O$, and the conclusion is drawn that this mineral is probably an impure boronatrocalcite, $NaCaB_5O_9,8H_2O$. Experiments in which boronatrocalcite and borax were heated, showed that at 60° the latter was transformed into $Na_2B_4O_7,5H_2O$, whilst at 63° the former lost water, giving $NaCaB_5O_9,4H_2O$. The upper temperature limit of the existence of boronatrocalcite is therefore lower than that previously recorded, and the formation of colemanite from boronatrocalcite at about 65° according to the equation $2NaCaB_5O_9,8H_2O = Na_2B_4O_7,5H_2O + Ca_2B_6O_{11},5H_2O + 6H_2O$ implies superheating of the latter. In the presence of sodium chloride, borax, potassium chloride, and glaserite, boronatrocalcite decomposes at 51°. van't Hoff has also been unsucessful in preparing borocalcite, $CaO,2B_2O_3,4H_2O$, artificially, and specimens preserved in various collections proved on examination to be boronatrocalcite, pandermite, &c. The deposit formed on heating at 40° a solution of lime and boric acid had approximately the composition of borocalcite, but was not homogeneous. The same solution heated to 83° deposited colemanite, and this appears to be the most convenient method of synthesising the mineral. As these experiments have completed the investigation of the natural calcium borates, the results obtained have been embodied in a diagram. Turning now to the magnesium compounds, it was found that ascharite has the formula $2MgO,B_2O_3,H_2O$.

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[1] *Abstr.*, 1907, ii, 363, 702.

A consideration of the mode of occurrence of this mineral suggested that it could be probably prepared from pinnoite, $MgO,B_2O_3,3H_2O$, and on heating this substance for eight days at 150° with a saturated solution of sodium chloride a deposit was obtained of which the composition and properties were the same as those of ascharite. These borates are hard to prepare, and it has been noticed that the difficulty of synthesising the minerals of the salt deposits increases as we pass from the chlorides to the sulphates and on to the borates, whilst, as regards salts of the same acid, those of the alkaline earths are harder to obtain than those of the alkalis. This phenomenon may be given a quantitative expression, and the various compounds may be arranged in order of their "mean valence," when it is found that salts for which the numerical value of the mean valence is low are easier to prepare than those for which it is high. The number to which the term mean valence is applied is a quotient obtained from the formula of the compound as follows; the numerator is formed by adding certain values assigned to each of the constituents of the compound, and the denominator by adding certain other values assigned to the same constituents. Thus in the numerator, Na, K, and $Cl = 1$, Ca, Mg, and $SO_4 = 2$, $B_2O_3 = 6$, and $H_2O = 4$. In the denominator, Na, K, Cl, Ca, Mg, and $SO_4 = 1$, $B_2O_3 = 2$, and $H_2O = 3$. As an example, we may calculate the "mean valence" for glauberite, $CaNa_2(SO_4)_2$: we have $2 + 2 + 4 \div 1 + 2 + 2 = 1{\cdot}6$. Again for ascharite, $2MgO,B_2O_3,H_2O$, we have $4 + 6 + 4 \div 2 + 2 + 3 = 2$, whilst for Glauber's salt, $Na_2SO_4,10H_2O$, the value is 1·33. The low number obtained in the last case is in harmony with the ease with which it can be prepared, whilst the high value calculated for ascharite indicates that it can only be synthesised with difficulty. In this connexion, attention may be called to a new method of expressing van't Hoff's results developed by Jänecke[2] in several recent papers.

Silicate Fusions.—Reference was made last year[3] to the important paper in which J. H. L. Vogt expounded his views on the nature of silicate fusions. The continuation[4] then promised has since appeared, and contains an exhaustive discussion of the phenomena of crystallisation in the case of granitic eruptive magmas. The composition of the binary eutectics, quartz-orthoclase and quartz-albite, and of the ternary eutectic, quartz-orthoclase-albite (or plagioclase), are dealt with in detail. Incidentally it is pointed out that pressure appears to have but little influence on the composition of the quartz-felspar eutectic. The conclusion is arrived at that the phenomena of crystallisation in the case of the acid eruptive rocks can be satisfactorily accounted for on a physico-chemical basis.

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[2] *Abstr.*, 1906, ii, 833; 1907, ii, 278, 480, 702.

[3] *Ann. Report*, 1906, 301.

[4] *Tsch. Min. Mitt.*, 1907, **25**, 361.

The order of separation and mutual relations of binary and ternary mixtures of diopside, anorthite, nepheline, orthoclase, and magnetite have been studied by R. Freis.[5] Silicates of definite composition, prepared artificially, were fused together and the melting points of the glasses and of the crystallised products were determined. The methods of experimenting were similar to those employed by M. Vučnik and H. H. Reiter.[6] The order of separation was found to follow Rosenbusch's rule, and the conclusion was arrived at that dissociation takes place in these silicate fusions and that the laws which hold for dilute solutions are not applicable.

Electric Conductivity of Silicates.—C. Doelter[7] has examined the electric conductivity of silicates between 500° and 1400°. Above 500°, all silicates conduct a little, and as the temperature rises the conductivity increases. The melting point is a more or less well-defined transition point in the temperature-conductivity curve, especially in the case of those silicates which have a sharp melting point. In the fused state, the temperature-coefficient is inconsiderable. Silicates which crystallise on solidification show a notable change of conductivity at the solidifying point, whilst those which give glasses show no such marked change. At sufficiently high temperatures, silicates conduct much like aqueous solutions. Orthoclase and augite were found to conduct better than plagioclase felspars and hornblende.

Law of Rosenbusch.—The law formulated by Rosenbusch, that in the eruptive rocks the sum of the molecular numbers approaches 155, has been the subject of consideration by E. Sommerfeldt,[8] who expresses it as follows: for any two eruptive rocks A and B, the sum of the individual oxides is such, that equal numbers of gram-molecules of the oxides exist in A and in B. This approximately constant number is termed by Sommerfeldt the "topic" number, and is obtained by adding the numbers got on dividing the percentage of the several oxides by their molecular weights. In the case of an individual mineral, the result may be reached more readily by dividing the coefficients of the oxides composing it by the molecular weight of the mineral and adding the results. To explain the law enunciated by Rosenbusch, Sommerfeldt assumes that the minerals which replace one another during alterations in the concentration of the magma of eruptive rocks possess similar ("simultan") composition and approximately equal molecular weights; two silicates being said to be similar if their formulæ can be so written that in the acid radicle of the first the silicon offers as many valencies to the oxygen as in the acid radicle of the second, whilst the basic radicles agree in the sum of their valencies. Two salts of the same silicic acid are always similar, but similar salts need not come from like acids; thus orthoclase comes from $H_4Si_3O_8$ and anorthite from $H_8Si_2O_8$, but $H_4Si_3O_8$ may be regarded as H_4Si,Si_2O_8. Anorthite is written by Sommerfeldt, $Al(O/2)_3CaOAl(O/2)_3Si_2O_4$, and orthoclase, $K(O/2)Al(O/2)_3SiO_2Si_2O_4$; in both cases, the sum of the coefficients of the oxides is 4, and, since the molecular weights are nearly equal, the topic numbers are also nearly equal. Applying these principles to other rock-forming minerals, the gram-molecule of nepheline is taken to be represented by $(AlNaSiO_4)_2$. Leucite is considered as made up of orthoclase and nepheline, 1 gram-molecule of the former uniting with $\frac{1}{2}$ gram-molecule of the latter to form $1\frac{1}{2}$ gram-molecules of leucite. Hence for these two minerals the topic numbers are the same as in the case of the felspars. Similar considerations may be applied to the pyroxenes, amphiboles, and micas, and for these minerals the topic numbers calculated by Rosenbusch's method give results ranging from 143 to 182 in the case of the pyroxenes (22 analyses, the average value being 166), from 143 to 177 in the case of the amphiboles (9 analyses, average value 166), and from 165 to 169 in the case of the micas.

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[5] *Abstr.*, 1907, ii, 183.

[6] *Ann. Report*, 1906, 301.

[7] *Anzeiger K. Akad. Wiss. Wien.*, 1907, 289.

[8] *Centr. Min.*, 1907, 2.

Artificial Formation of Minerals.

Interesting results have been obtained in attempts to synthesise the natural sulphates of iron and to crystallise sulphates of the alkaline earths.

Barytes Group.—P. Gaubert[9] has found that $BaSO_4$, $SrSO_4$, $PbSO_4$ and $CaSO_4$ can be obtained well crystallised in forms like those observed in nature by evaporating solutions of these sulphates in concentrated sulphuric acid. On evaporating solutions containing mixtures of any two of the first three sulphates, mixed crystals were obtained, but attempts to form mixed crystals containing $CaSO_4$ and one of the other sulphates were unsuccessful. Crystals of $BaSO_4$, of $SrSO_4$, and of $CaSO_4$ prepared in this way have also been studied by Sommerfeldt,[10] who has made the interesting observation that calcium sulphate gives crystals exhibiting faces which cannot be brought into harmony with the axial ratios of anhydrite, although they are comparable with prominent forms found on barytes. Calcium sulphate appears therefore to be dimorphous, crystallising as anhydrite, and also in this new labile form, for which the name metahydrite is proposed. A variety of calcium sulphate found at Santorin possibly represents a natural occurrence of this variety. It is worthy of note that the density, cleavages, and optical characters of metanhydrite are the same as those of anhydrite, the two substances being dimorphous only as regards external form.

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[9] *Compt. rend.*, 1907, **144**, 877.

[10] *Abstr.*, 1907, ii, 703.

Coquimbite.—R. Scharizer[11] has prepared coquimbite, $Fe_2(SO_4)_3,9H_2O$, by dissolving ferric hydroxide in excess of sulphuric acid. On evaporation and after standing for a long time in the air, a mixture of coquimbite with acid ferric sulphate is obtained, from which, by washing with alcohol, the former can be isolated in hexagonal plates, optically uniaxial and positive. The substance thus prepared agrees closely in composition and properties with the natural mineral. When dehydrated by heating in a test-tube, a thermometer being placed in the powder, the temperature remains stationary for a time at 100° and again at about 124°, 6 molecules of water being lost up to 100° and 7 at the higher temperature. A neutral solution of coquimbite deposits a mixture of copiapite, $Fe_4S_5O_{21},18(\text{or }16)H_2O$, with the acid ferric sulphate, $Fe_2(OH)_2(SO_4H)_4,6H_2O$. Owing to this behaviour, the formula $SO_4[Fe(OH)SO_4H]_2,7H_2O$ is proposed for coquimbite. Scharizer has also studied the behaviour of roemerite when exposed to moist air, and finds that it decomposes into a mixture of ferrous and ferric sulphates, the latter giving copiapite and acid sulphate.

Hæmatite.—Fine crystals of hæmatite have been noted by C. E. Monroe[12] in the interior of the iron pipes of the heater in an apparatus for producing chlorine by Deacon's process. The crystals have been formed by the action of the hydrochloric acid on the iron, giving iron chloride, and the subsequent conversion of this into oxide by air passed through the pipes. The size of the crystals varies with the diameter of the pipe in which they were formed. The largest, 3 cm. across, were found in a 20-inch pipe.

New Minerals.

Benitoite.—This exceedingly interesting mineral occurs in colourless to blue, transparent, rhombohedral crystals of trigonal-pyramidal habit (combinations of trigonal prisms and pyramids with the basal plane), associated with a soda zeolite, in veins in a basic igneous rock or highly altered schist near the head waters of the San Benito River in San Benito Co., California. G. D. Louderback[13] states that the hardness, whilst greater than that of orthoclase and labradorite, is less than that of chrysolite and quartz. The indices of refraction for sodium light are 1·77 (ord.) and 1·80 (extr.). The pleochroism of the mineral is very strong (ω colourless, ϵ blue), and taken in conjunction with its other physical characters and beautiful colour renders it suitable for use as a gem stone. It is very slowly attacked by molten potassium hydrogen sulphate, and is practically insoluble in hydrochloric acid. It is, however, readily decomposed by hydrofluoric acid.

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[11] *Abstr.*, 1907, ii, 482.

[12] *Amer. J. Sci.*, 1907, [iv], **24**, 485.

[13] *Abstr.*, 1907, ii, 705.

The formula $BaTiSi_3O_9$ has been deduced from the mean of two concordant analyses by W. C. Blasdale :

SiO_2.	TiO_2.	BaO.	Total.	Sp. gr.
43·68	20·09	36·33	100·10	3·64—3·65

Blandfordite is a monoclinic pyroxene described by L. L. Fermor.[14] It exhibits strong pleochroism (rose-pink to sky-blue), and contains some sodium, manganese, and iron.

Blomstrandine.—This name (not to be confused with blomstrandite) has been assigned by Brögger[15] to a mineral found in fine black, orthorhombic crystals at Hitterö (analysis I), and also in the neighbourhood of Arendal (analysis II) and elsewhere. The analyses made by Blomstrand show that it is a titano-columbate of yttrium earths ; æschynite, to which it is closely related crystallographically, being the corresponding cerium salt. Chemically, it is very similar to polycrase, and it is possible that the two minerals are related to one another in much the same way as pyroxene and amphibole :

	Cb_2O_5.	Ta_2O_5.	TiO_2.	SnO_2.	SiO_2.	ZrO_2.	UO_2.	ThO_2.	$(Y,Er)_2O_3$.	$(Ce,La,Di)_2O_3$.
I.	17·99	0·89	32·91	0·12	0·38	trace	4·01	7·69	28·76	1·97
II.	23·35	1·15	27·39	0·18	0·40	1·33	5·35	4·28	25·62	2·48

	FeO.	MnO.	CaO.	ZnO.	PbO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
I.	1·48	0·27	1·02	—	0·06	0·04	0·22	0·19	1·88	99·88	4·93—4·82
II.	1·43	0·30	1·80	0·09	0·84	0·15	0·90	0·18	2·56	99·78	4·91

Carbapatite.—See Podolite (page 287).

Carlosite.—A black or brownish-black, prismatic mineral, apparently monoclinic, occurs associated with benitoite. As its characters do not appear to agree with those of any known species, the name carlosite has been proposed for it by Louderback.[16] Its chemical composition is as yet undetermined.

Davidite.—D. Mawson[17] has described the occurrence of heavy, black minerals in pegmatitic veins near Olary, S. Australia. One of these, for which the name davidite has been suggested, is found in scattered grains and cuboid crystals remarkable for their very brilliant lustre and glassy fracture. The specific gravity is about 4. A qualitative examination by E. H. Rennie and W. T. Cooke has shown that it contains more than 50 per cent. of titanium oxide, a large quantity of iron, and notable amounts of rare earths, uranium, vanadium, and chromium. Small quantities of radioactive carnotite and of a mineral which appears to be roscoelite have been found in the same veins.

Georgiadesite.—This new mineral, described by A. Lacroix[18] and A. B. de Schulten, is found lining cavities in a vitreous scoria surrounding fragments of charcoal and wood at the ancient mines of Laurion. It is associated with laurionite, fiedlerite, and matlockite. The crystals are orthorhombic, but resemble hexagonal prisms. The analytical results agree well with the formula $Pb_3(AsO_4)_2,3PbCl_2$:

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[14] *Abstr.*, 1907, ii, 701.
[15] *Ibid.*, 884.
[16] *Ibid.*, 705.
[17] *Trans. Roy. Soc. S. Australia*, 1906, **30**, 188.
[18] *Abstr.*, 1907, ii, 971.

As_2O_5.	PbO.	Pb.	Cl.	Total.	Sp. gr.
12·49	38·86	36·38	12·47	100·20	7·1

Hollandite.—In the course of a comprehensive account of the Indian manganese-ore deposits,[19] Fermor has described a new mineral found at Kájlidongri, Jhábua State, Central India. It occurs in black, pseudo-tetragonal crystals, showing perfect prismatic cleavages and shining metallic lustre. The formula $m(Ba,Mn)_2MnO_5 + nFe_4(MnO_5)_3$ has been deduced from the following analysis by H. J. Winch:

Fe_2O_3.	Al_2O_3.	MnO_2.	MnO.	BaO.	SiO_2.	Total.	Sp. gr.
10·56	0·94	65·63	5·12	17·59	trace	99·84	4·95

A similar mineral occurs as cleavage masses at Sitapár, Chhindwára District, Central Provinces.

Irvingite is a new variety of lithia-mica found in the pegmatite veins near Wausau, Wisconsin. It is described by S. Weidman[20] as occurring in crystals about an inch across, grey to yellow or pinkish-white in colour. The axial angle is apparently rather larger than in the case of lepidolite and zinnwaldite. In addition to a good basal cleavage, many of the crystals show a well-marked prismatic parting. An analysis of pure material made by V. Lenher gave the following results:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	Li_2O.	F.	H_2O (110°).	H_2O (ign.)
57·22	0·14	18·38	0·32	0·53	0·09	0·20	9·12	5·14	4·46	4·58	0·42	1·24

This mica differs from polylithionite in containing more alumina and less fluorine, the proportions of the alkalis are also different. From cryophyllite, zinnwaldite, and lepidolite, it is distinguished by its higher content of silica and soda. The formula may be written as a trisilicate, $3Si_2O[Al,(F,OH)]''O,R_2'O$, or, according to F. W. Clarke's theory of the mica group, as $R_2'AlX(F,OH)$, where X represents Si_3O_8 and SiO_4 in the ratio 4 : 1.

Marignacite is a variety of pyrochlore found in small, regular, brown octahedra associated with quartz, alkali-felspar, and acmite in pegmatite near Wausau, Wisconsin. The mineral is very refractory towards acids, and is only slightly attacked when fused with sodium carbonate. It can, however, be decomposed by hydrofluoric acid or by fusion with potassium hydrogen sulphate. An analysis made by methods fully described, gave Weidman and Lenher[21] the following results:

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[19] *Abstr.*, 1907, ii, 701.

[20] *Ibid.*, 630.

[21] *Ibid.*, 482.

Cb_2O_5.	Ta_2O_5.	SiO_2.	TiO_2.	Fe_2O_3.	FeO.	Ce_2O_3.	Y_2O_3.	ThO_2.
55·22	5·86	3·10	2·88	0·50	0·02	13·33	5·07	0·20

CaO.	MgO.	Na_2O.	K_2O.	H_2O above 110°.	H_2O below 110°.	Total.
4·10	0·16	2·52	0·57	5·95	0·45	99·93

Al_2O_3, MnO, SnO_2, WO_3, Di_2O_3, La_2O_3, Er_2O_3 occur in traces, but F, ZrO_2, BeO, UO_2, Li_2O could not be detected. The presence in this pyrochlore of silica and titanium oxides apparently as normal constituents, together with its high content of cerium oxide, indicates relations to the columbate-tantalates, on the one hand, and to titano-silicates, on the other. Fluorine, which occurs in many pyrochlores, is here doubtless replaced by hydroxyl.

Metanhydrite.—See page 282.

N'hangellite.—This variety of bitumen from Portuguese East Africa has been described by Sir B. Redwood.[22] It is allied to coorongite.

Palmierite.—In a long and interesting account of the minerals derived from the fumaroles of the eruption of Vesuvius, in April, 1906, A. Lacroix[23] has described a new species which occurs imbedded in crusts of aphthitalite, $(K,Na)_2SO_4$. On removal of the aphthitalite by treatment with cold water, minute, micaceous lamellæ of hexagonal outline are left. These lamellæ, to which the name palmierite has been given, are uniaxial and exhibit strong negative double refraction. The mineral is anhydrous, and its specific gravity is greater than 3·3. It is decomposed by hot water, leaving a residue of anglesite. An analysis by Pisani gave the following results:

SO_3.	PbO.	K_2O.	Na_2O.	NaCl.	Insol.
21·80	40·65	9·10	2·60	2·64	22·59

Lacroix believes that if allowance is made for the insoluble residue, which consists in the main of hæmatite, and if the sodium chloride present is regarded as an impurity, that the above data lead to the formula $(Na,K)_2SO_4,PbSO_4$. The divergence between the calculated and the observed numbers is, however, so great that this formula can only be regarded as conjectural. The numbers published by Lacroix are more in harmony with a formula $Na_2SO_4,2K_2SO_4,4PbSO_4$.

It is interesting to notice that a crystalline compound having the same physical properties can be obtained by fusing lead sulphate with a considerable excess of alkaline sulphates.

Parahopeite.—Associated with tarbuttite from Broken Hill mines, North-Western Rhodesia, occurs another species of the same chemical composition as hopeite which has been termed parahopeite by L. J. Spencer.[24] The platy crystals somewhat resemble hemimorphite in appearance, but are anorthic. They have one perfect cleavage approximately perpendicular to the plates through which emerges one of the optic axes.

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[22] *Abstr.*, 1907, ii, 698.

[23] *Ibid.*, 628.

[24] *Nature*, 1907, **77**, 143.

Podolite.—Minute, hexagonal crystals occur in cavities in the phosphorite nodules from the district of the river Uschitza, Govt. Podolia, S. Russia. The crystals somewhat resemble apatite, and exhibit similar optical anomalies, but the birefringence is greater; the mean index of refraction is 1·635 and the specific gravity is 3·077. The analysis quoted below shows that the composition must be represented as $3Ca_3(PO_4)_2,CaCO_3$, an apatite with $CaCO_3$ replacing $Ca(F,Cl)_2$. W. Tschirwinsky[25] proposes to call this mineral podolite, and P. Tschirwinsky has accordingly withdrawn the name carbapatite, which he had previously suggested for a substance of similar composition:

CaO.	Fe_2O_3.	P_2O_5.	CO_2.	Total.
51·15	3·04	39·04	3·90	97·13

Priorite.—Brögger[26] has proposed this name for a titano-columbate of yttrium, cerium, &c., found in the tin gravels of Swaziland, South Africa, and analysed by Prior.[27] The mineral occurs in indistinct, orthorhombic crystals, isomorphous with blomstrandine and dimorphous with euxenite, the four minerals, euxenite-polycrase and priorite-blomstrandine, forming an isodimorphous group.

Quisqueite.—This name has been suggested by F. Hewett[28] for a remarkable compound of sulphur and carbon, resembling asphaltite in appearance, found associated with patronite (see page 302). A sample, analysed by Hillebrand, had the following composition:

S (sol. in CS_2).	S (comb.).	C.	H.	N.	O (diff.).	H_2O at 110°.	Ash.	Sp. gr.
15·44	31·17	42·81	0·91	0·47	5·39	3·01	0·80	1·75

At present, nothing is known as to the chemical structure of this substance.

Reyerite.—(See page 288).

Rhönite.—In basalts from the Rhön Mountains and from several other localities, Soellner[29] has observed a brown mineral which was at first believed to be ænigmatite. As, however, the composition proved on analysis to be quite different from that of ænigmatite, the name rhönite has been proposed for it. The mineral is triclinic, and appears to be isomorphous with ænigmatite, which it resembles closely in habit, twinning, and cleavage. In thin sections, it exhibits strong absorption and pleochroism. The formula

$$(Ca,Na_2,K_2)_3Mg_4Fe_2''Fe_2'''Al_4(Si,Ti)_6O_{30}$$

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[25] *Abstr.*, 1907, ii, 481.
[26] *Ibid.*, 884.
[27] *Ibid.*, 1899, ii, 433.
[28] *Ibid.*, 789.
[29] *Ibid.*, 1907, ii, 972.

is based on the following analysis by Dittrich:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	Total.
24·42	9·46	17·25	11·69	11·39	trace	12·62	12·43	0·67	0·63	100·56

Spandite.—Fermor[30] has suggested this name for a garnet, intermediate in composition between spessartite and andradite.

Strüverite.—This interesting mineral occurs in pegmatite near Craveggia, N. Piedmont. It is black and opaque, and has been shown by Zambonini[31] to crystallise in the tetragonal system. In habit and angles it is very similar to rutile, tapiolite, mossite, and ilmenorutile. The analysis of the mineral was undertaken by Prior, who has found that its composition can be represented by the formula $FeO,(Ta,Cb)_2O_5,4TiO_2$.

Turbuttite is a basic zinc phosphate, $Zn_3P_2O_8,Zn(OH)_2$, found by L. J. Spencer[32] associated with lead and zinc ores on a bone-breccia from the Broken Hill mines, North-Western Rhodesia. The crystals are anorthic, and show a perfect cleavage. The mineral, which is abundant, is readily distinguished from hopeite and parahopeite by its high specific gravity, 4·15.

Tschernichewite.—This name has been given by Duparc and Pearce[33] to a variety of amphibole found as small, acicular crystals in a quartzite near Verkne-Tschouwal, in the Northern Urals. It is defined by its optical characters, and appears to be rich in iron and sodium.

Winchite is also a variety of amphibole. It has been described by Fermor,[34] and is closely allied to tremolite.

New Yttrium Columbium Mineral.—Hauser[35] has analysed a mineral as yet unnamed, which will be seen from the following figures to be essentially a yttrium columbate:

	Cb_2O_5.	TiO_2.	Y_2O_3.	$La(Ce,Di)_2O_3$.	Al_2O_3.	Fe_2O_3.	CaO.	PbO.	SnO_2.	ThO_2.	Ign. loss.
I.	38·52	6·48	36·99	4·01	0·98	2·34	1·93	0·26	trace	trace	8·76
II.	45·23		41·19		0·80	2·51	1·80	0·19	trace	trace	8·40

Micaceous Zeolites.—Cornu[36] proposes to group under this name gyrolite and zeophyllite together with two new minerals, one termed reyerite, and the other as yet unnamed. The group is defined as consisting of hydrated calcium silicates with or without fluorine, crystallising in the rhombohedral system, and exhibiting very similar cleavages and optical properties. The individual members may be distinguished by their specific gravities and indices of refraction as well as by their composition, as will be seen from the following table, in which are given partial analyses of gyrolites (I, from Skye; II, from Poonah; III, from Böhmisch-Leipa), of zeophyllite from Radzein (IV), and of reyerite from Greenland (V):

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[30] *Rec. Geol. Surv. India*, 1907, **35**, 22.

[31] *Abstr.*, 1907, ii, 364.

[32] *Nature*, 1907, **77**, 143.

[33] *Abstr.*, 1907, ii, 484.

[34] *Ibid.*, 701.

[35] *Ibid.*, 704.

[36] *Ibid.*, 483.

	SiO_2.	CaO.	Al_2O_3.	MgO.	F.	H_2O.	Sp. gr.	$\mu(\omega)$.
I.	51·99	32·02	—	—	—	12·80	2·420	1·54—1·55
II.	52·63	32·23	—	—	—	12·96	2·342—2·410	1·546
III.	52·89	32·35	—	—	—	13·06	2·397	1·542
IV.	38·82	43·44	2·16	0·26	9·48	8·56	—	—
V.	53·31	32·22	3·27	—	—	6·73	2·499—2·578	1·564

Mineral Analyses.

Great activity has been displayed during the past year in the making of mineral analyses, and much light has been thrown on the composition of rare species. The most noteworthy results are those brought together by Brögger in his great monograph[37] on the columbates, tantalates, and titanates from the Norwegian pegmatite veins, of which the first part was published towards the close of 1906. The posthumous paper of S. L. Penfield on the composition of the amphiboles also deserves especial notice, whilst all who are interested in mineral analysis will welcome the publication by Hillebrand[38] of a revised edition of his memoir on the analysis of silicate and carbonate rocks. In the following pages, reference will be made to those analyses which are important because made on selected material of which the physical characters have also been carefully determined, or which throw light on the composition of species the nature of which has hitherto been imperfectly understood.

Amphibole Group.—The views commonly held at the present time as to the composition of this important and perplexing group of minerals are those due to Tschermak and Rammelsberg respectively. According to the former, tremolite, the simplest member of the group, is $CaMg_3Si_4O_{12}$, and green actinolite is $Ca(Mg,Fe)_3Si_4O_{12}$. In amphiboles containing sesquioxides, the existence of molecules, $(Ca,Mg)_2Al_4Si_2O_{12}$ or $(Ca,Mg)_2Fe_4Si_2O_{12}$, is assumed, and the occurrence of alkalis in certain varieties is ascribed to the presence of $Na_2Al_2Si_4O_{12}$ or the analogous potassium compound. The latter regards the amphiboles as metasilicates, $R''SiO_3$ ($R = Ca$, Mg, Fe, Mn, Na_2, K_2) *plus* varying proportions of Al_2O_3 and Fe_2O_3. It had long been the intention of the late S. L. Penfield to undertake an exhaustive investigation of the group, and after his death a manuscript was discovered in his desk in which were given analyses of twelve varieties of amphibole. This manuscript has now been published,[39] and will long rank as a contribution of the first importance to the chemistry of this group. The material was selected with the greatest care, and, by fractionating by means of a heavy liquid, was obtained in the highest possible state of purity. The analyses were carried out by F. C. Stanley under Penfield's direction according to the methods described in the publications of Hillebrand and Washington. The most important result has been the demonstration of the invariable occurrence in these minerals of considerable amounts of water (of constitution) together with appreciable quantities of fluorine. The part played by these two constituents, unaccounted for by the theories of Tschermak and Rammelsberg, has been discussed by Penfield with characteristic acumen. The number of the constituents and the diversity of composition met with in the group lead him to suggest that its members possess a complex structure. Owing to the so-called "mass effect" of such complex structures, H_2O, Na_2O, CaO, MgO, Al_2O_3, which are not isomorphous in simple compounds, appear to enter the molecule as isomorphous constituents. A confirmation of this view is to be found in the fact that amphiboles when fused break up into simpler substances; they are, moreover, exceedingly difficult to prepare artificially, and apparently require for their formation high pressure as well as high temperature. Regarding the acid as the factor controlling the similar crystallisation of these substances, Penfield suggests the possible existence of an amphibole ring derived from a metasilicic acid, $H_8Si_4O_8$. The specimens analysed fall naturally into three groups. The first consists of two tremolites and four actinolites, the former from Richville, near Gouverneur, New York (I), and from Lee, Massachusetts (II), and the latter from Greiner, Tyrol (III), from Russell, St. Lawrence Co., New York (IV), from Kragerö, Norway (V), and from Pierrepont, St. Lawrence Co., New York (VI). The ratios obtained are given in the following table, where TiO_2 is included with SiO_2, $R_2'''O_3$ represents Al_2O_3 and Fe_2O_3, and R″ in R″O stands for Fe, Mn, Mg, Ca, K_2, Na_2, and H_2:

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[37] *Abstr.*, 1907, ii, 884.

[38] *United States Geol. Surv.*, 1907, *Bull.*, 305.

[39] *Abstr.*, 1907, ii, 102.

	SiO_2	:	$R_2''O_3$	:	$R''O + F_2$.
I.	0·957	:	0·014	:	0·958
II.	0·963	:	0·018	:	0·954
III.	0·938	:	0·017	:	0·935
IV.	0·914	:	0·041	:	0·908
V.	0·880	:	0·059	:	0·874
VI.	0 876	:	0·045	:	0·923

It will be noticed that the ratio $SiO_2 : R''O + F_2$ is almost exactly 1 : 1. In a general way, this result is in harmony with the views of Rammelsberg and of Tschermak. The former, however, makes no provision for fluorine, and the assumption by the latter that sodium is present as $Na_2Al_2Si_4O_{12}$ is untenable, for were this so the above ratio 1 : 1 would not hold. The presence of fluorine, tervalent oxides, and hydroxyl can, however, be accounted for if the existence of bivalent groupings of the type ·AlF·O·FAl· and ·Al(OH)·O·(OH)Al·, or, as they may be written, $[R_2'''O(F,OH)_2]''$, are admitted playing parts similar to those which have been shown to be filled by $(MgF)'$ and $(Mg,OH)'$ and by $(AlF)''$ or $(Al,OH)''$ in a large number of minerals. It is, moreover, interesting to notice that, although the formulæ of tremolite and of actinolite have long been written $CaMg_3Si_4O_{12}$ and $Ca(Mg,Fe)_3Si_4O_{12}$ respectively, yet in the specimens analysed the sum Mg + Fe + Mn always falls far short of 75 per cent., the figures, in fact, being remarkably constant in the neighbourhood of 65 per cent. The calcium again, taken alone, never quite replaces 25 per cent. of the total hydrogen of the metasilicic acid, but, if the small amounts of sodium and potassium present be added, this total is reached or slightly exceeded, whilst after deducting hydrogen present as OH in the hypothetical group $[R_2'''O(F,OH)_2]''$ a considerable, but variable, excess of unreplaced hydrogen remains, which in analysis III amounts to 9 per cent.

The second group includes hornblendes from Renfrew, Ontario (VII), from Edenville, Orange Co., New York (VIII), from Cornwall, Orange Co., New York (IX), and from Monte Somma (X). These all differ widely in composition from those of the group just considered. They show high percentages of sesquioxides and considerable amounts of alkalis, and are characterised by exhibiting an excess of $R''O$ over that required to satisfy the ratio $R''O : SiO_2 = 1 : 1$. As the actinolite from Pierrepont shares this peculiarity, it is perhaps to be regarded as a transition stage between the tremolites and hornblendes. In order to derive all these varieties from the same acid, Penfield finds it necessary to assume the existence in them of an additional bivalent group of the type ·Al(ONa)·ORO·(NaO)Al·, where R = Mg,Fe, somewhat similar to that already introduced to account for the presence of fluorine, OH, and sesquioxides in the tremolites. When this is done, the composition of these hornblendes can be satisfactorily represented with the exception of that from Monte Somma. In this case, the amount of water is small, and only a trace of fluorine is present. It therefore seems necessary to assume the presence of yet another bivalent radicle of the type $R''(OAl)_2O$. It is noteworthy that in all these compounds the calcium helped out by small quantities of sodium or potassium replaces one-quarter of the total number of hydrogen atoms of the acid just as it did in the tremolite group.

Two of the hornblendes examined stand apart from the rest. One of these is the well-known black, basaltic hornblende from Bilin, in Bohemia (XI), and the other is a light brown mineral from Grenville Township, Quebec (XII). Analysis of the Bilin crystals leads to the ratios $SiO_2 : R_2O_3 : RO = 3{\cdot}00 : 0{\cdot}95 : 3{\cdot}03$. This result is remarkable for its close approximation to the garnet ratios 3 : 1 : 3, and also because, unlike the hornblendes described above, the ratio $SiO_2 : RO$ is very nearly 1 : 1. To interpret this analysis, Penfield assumes the presence of a group like that introduced to explain the composition of the Monte Somma hornblende, but in applying it to the case of the Bilin crystals he proposes to double it, one R standing for Fe,Mg, and the other for Na_2,Ca. As the amount of fluorine is very small, it is unnecessary to assume the presence of any other radicle. The Grenville hornblende is remarkable for the large amounts of fluorine and alumina it contains. It is probable that in this case some of the fluorine is united with a bivalent metal, magnesium, for example, to form a radicle present in addition to the groups $[Al_2OF_2]''$ and $[Al_2O_4RNa_2]''$. In both varieties, we note once again that approximately one-quarter of the hydrogen of the acid is replaced by calcium.

The composition of individual amphiboles has been studied by several other workers. A. Lacroix [40] gives an analysis (XIII) made by F. Pisani of a hornblende from a block ejected by Vesuvius in the eruption of 1906. The crystals appear to be the same as those identified by Zambonini with the variety *catoforite*. Lacroix thinks, however, that they do not belong to this variety, but constitute a new type. Hornblendes from the hornblende-gneiss of Markirch (XIV*a*) and from the serpentine of the Rauenthal, Alsace (XIV*b*), have been analysed by A. Rhein.[41] In conclusion, we may note that the hornblende which forms the most important constituent of the essexite at Mount Johnson, Montreal, which was analysed by N. N. Evans [42] in 1903, has lately been the subject of a careful optical investigation by H. Tertsch.[43]

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	F.	Sp. gr.
I.	57·45	—	1·30	0·18	0·22	0·07	24·85	12·89	0·54	0·67	1·16	0·77	2·997
II.	57·69	0·14	1·80	0·00	0·55	trace	24·12	13·19	0·22	0·48	1·56	0·37	2·980
III.	56·25	0·00	1·24	0·78	5·50	0·48	21·19	12·08	0·28	0·19	1·81	0·04	3·047
IV.	54·80	0·10	2·58	2·50	4·75	trace	20·30	12·08	0·24	0·82	1·60	0·77	3·092
V.	51·85	1·26	4·36	2·58	5·46	0·35	19·48	10·60	0·35	2·15	1·21	0·46	3·137
VI.	52·31	0·28	2·69	3·09	6·68	0·70	19·27	11·88	0·50	0·78	1·42	0·93	3·111
VII.	43·76	0·78	8·33	6·90	10·47	0·50	12·63	9·84	1·28	3·43	0·65	1·82	3·290
VIII.	41·99	1·46	11·62	2·67	14·32	0·25	11·17	11·52	0·98	2·49	0·61	0·80	3·285
IX.	36·86	1·04	12·10	7·41	23·35	0·77	1·90	10·59	3·20	1·20	1·30	0·27	—
X.	39·48	0·30	12·99	7·25	10·73	1·00	11·47	12·01	2·39	1·70	0·76	0·50	3·286
XI.	39·95	1·68	17·58	7·25	2·18	trace	14·15	11·96	1·98	3·16	0·41	0·30	3·226
XII.	45·79	1·20	11·37	0·42	0·42	0·39	21·11	12·71	1·69	2·51	0·67	2·76	3·110
XIII.	41·50	2·42	6·60	12·32	5·30	—	15·89	11·70	1·85	2·33	0·37	0·45	3·18
XIV*a*.	51·60	—	5·04	2·84	4·67	—	23·75	10·28	—	—	1·84	—	2·97
XIV*b*.	51·75	—	5·20	2·64	4·52	—	23·80	10·31	—	—	1·54	—	—

Anapaite.—P. Tschirwinsky [44] has pointed out that anapaite may be regarded as a double salt composed of 1 molecule of vivianite, $Fe_3(PO_4)_2,8H_2O$, with 2 molecules of ornithite, $Ca_3(PO_4)_2,2H_2O$. He has also described several other minerals which occur in the Kerch and Taman peninsulas, South Russia, including one which may be new and to which the formula $100[Fe_2O_3,P_2O_5,2\frac{1}{2}H_2O]+18[Fe(OH)_3,3H_2O]$ is assigned.

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[40] *Nouv. Arch. Mus. Nat. Hist.*, 1907, [iv], **9**, 90.

[41] *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1907, **6**. 132.

[42] *Amer. J. Sci.*, 1903, [iv], **15**, 391.

[43] *Tsch. Min. Mitt.*, 1907, **25**, 457.

[44] *Abstr.*, 1907, ii, 364.

Anauxite.—This name was given by Breithaupt to a product of the weathering of augite from Berg Hradischt, near Bilin. These augite pseudomorphs have lately been re-examined by W. P. Smirnoff,[45] who has isolated the crystalline, birefringent anauxite from the cimolite with which it is mixed, and has analysed both substances. The results for anauxite, agree closely with those obtained for a similar mineral from Tschakwa, Caucasus, and lead to the formula $H_4Al_4Si_5O_{18},2H_2O$. The cimolite appears to be a product of the further change of anauxite. The formula $H_2Al_2Si_3O_{10},H_2O$ is deduced from the analytical results which agree well with those already obtained by R. Scharizer for the same substance.

Apatite.—The paragenesis, crystallography, optical characters, and chemical composition of the somewhat similar apatites from Epprechtstein, in Bavaria, and from Luxullian, in Cornwall, have been very carefully studied by K. Walter [46] with the special object of throwing light on the relations which exist between the indices of refraction of the mineral and its colour and composition. Under I is given the mean of two analyses of the Epprechtstein mineral. The rest of the analyses were of material from Luxullian; under II being given the results for blue crystals, under III the mean of two determinations made on yellow portions of blue crystals, and under IV the composition of yellow crystals which were blue in parts:

	Insol.	P_2O_5.	FeO.	Al_2O_3.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	F.	Cl.	H_2O.
I.	0·29	41·18	0·45	0·22	0·79	53·63	0·16	0·95	1·03	2·41	0·04	0·37
II.	0·27	41·16	0·21	0·19	0·39	54·03	0·15	1·11	1·07	2·60	0·07	0·35
III.	0·30	40·78	0·27	0·15	1·74	52·40	0·27	1·09	1·05	2·63	0·10	0·36
IV.	0·34	40·58	0·33	0·20	4·10	50·53	0·43	0·96	0·92	2·53	0·13	0·40

From the above table, it will be seen that both specimens are fluorapatites. The Epprechtstein variety, whilst in other respects similar to apatite from Minot, in Maine, is remarkable for its content in alkali. The interesting point about the Luxullian apatite is its variation in composition with colour, the yellow crystals containing more manganese and less calcium than the blue. In other respects, it resembles the Epprechtstein mineral, and, like it, contains more sodium and potassium than is usually met with. As the result of numerous measurements, Walter finds the mean axial ratio $a:c=1:0·73381$ for the Epprechtstein crystals, and 1 : 0·73357 for those from Luxullian. For the optical determinations, nine prisms were used (four Epprechtstein and five Luxullian). It was found that, although the indices of refraction vary considerably in different prisms from the same locality, the birefringence remains nearly the same. In both cases, the indices of refraction (in their lowest values) and the birefringence were less than those hitherto observed for apatite. The variations observed in the index do not seem to be connected with the colour of the crystals, but appear to depend rather on the composition, varying with the percentage of manganese present, as shown by the following determinations made on the material of which the composition is given above:

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[45] *Abstr.*, 1907, ii, 630.

[46] *Ibid.*, 481.

	I.	II.	III.	IV.
ω.Na	1·6338	1·6337	1·6375	1·6426
ϵ.Na	1·6323	1·6322	1·6359	1·6409

Baddeleyite.—The discovery of three crystals of this mineral in gem gravel from Balangoda, Ceylon, has afforded G. F. H. Smith[47] an opportunity for a fresh study of the crystallography of this interesting substance. One crystal was analysed by G. S. Blake and proved to be nearly pure zirconia.

Chloralluminite.—Scacchi observed the occurrence of aluminium chloride at Vesuvius, in 1872, and it has been found in considerable abundance by A. Lacroix[48] among the products of the acid fumeroles of the eruption of 1906. By a comparison of the forms and optical characters of the rhombohedral crystals with those of $AlCl_3,6H_3O$ prepared artificially, the composition and individuality of the species has been established.

Chloromanganokalite.—A. Lacroix[49] has given further details of this new mineral of which a preliminary account was published by Johnston-Lavis last year. Lacroix finds that the crystals are really oblique, although they resemble hexagonal prisms terminated by rhombohedra. He agrees with Johnston-Lavis in thinking that the mineral is a double chloride of manganese and potassium, but asserts that it is an anhydrous compound.

Columbite.—The crystallography of this mineral has been described in detail by Brögger,[50] and two analyses by C. W. Blomstrand of specimens from Ånneröd (I) and Fuglevik (II) have been published. A comparison with columbite from other localities indicates that the *a*-axis increases slightly and the *c*-axis decreases with an increase in the amount of tantalum present:

	Cb_2O_5.	Ta_2O_5.	SnO_2.	SiO_2.	FeO.	MnO.	CaO.	Loss on ignition.
I.	72·37	5·26	0·67	—	15·04	5·97	0·58	—
II.	71·38	5·87	0·51	0·17	15·86	5·33	0·80	0·12

Dimorphite.—J. Krenner[51] has examined small crystals having the composition As_4S_3 prepared by A. Schuller, who made them by melting together realgar with excess of arsenic dust and subsequent sublimation in a vacuum. The crystals so obtained are orthorhombic and tabular in habit ; a prismatic development can be got from solution in carbon disulphide. According to Schuller, this substance also appears capable of existence in another unstable modification. The chief interest of these observations lies in their bearing on the question of the existence of a mineral species termed dimorphite by A. Scacchi, who obtained it from the Solfatara, near Naples. He described the mineral as existing in two dimorphous forms having axial ratios, which could not be harmonised with one another or with those of orpiment. The latter is, moreover, readily distinguished from the two former by its excellent cleavage. The formula given by Scacchi was As_4S_3. The species was accepted at the time, but doubt was afterwards thrown on its individuality by Kenngott and by E S. Dana, who asserted its probable identity with orpiment. A comparison of the measurements made on Schuller's artificial crystals with those given by A. Scacchi for crystals of his second type have convinced Krenner that dimorphite must be regarded as a well-defined species.

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[47] *Abstr.*, 1907, ii, 702.

[48] *Bull. Soc. franç Min.*, 1907, **30**, 254.

[49] *Ibid*, 243.

[50] *Abstr.*, 1907, ii, 884.

[51] *Zeitsch. Kryst. Min.*, 1907, **43**, 476.

Danburite.—The following analysis by Tamura of well-crystallised danburite from Japan has been published by N. Fukuchi :[52]

SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
48·87	25·73	0·89	0·12	14·47	7·67	0·77	0·96	0·58

Datolite.—Good crystals from Japan have been found by Tamura to have the following composition :[53]

SiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
38·22	18·24	0·07	0·34	35·33	0·38	trace	0·01	7·86

Dolomite.—The important problems presented by the occurrence of this mineral have been discussed at considerable length by Pfaff.[54] Finding by a comparison of a number of analyses that magnesium limestones containing from 7 to 11 per cent. of $MgCO_3$ are very rare, if, indeed, they occur at all, whereas those containing up to 7 per cent. of $MgCO_3$ and from 11 to 46 per cent. of $MgCO_3$ are common, Pfaff proposes to reserve the name dolomite for the latter. After giving a résumé of the literature bearing on dolomitisation, and an account of what is known as to the solubility of dolomite and its artificial formation in the laboratory, he describes some experiments of his own. These deal with the action of solutions of magnesium sulphate or chloride on calcium carbonate and anhydrite in the presence of sodium chloride under pressures ranging from 40 to 200 atmospheres. With dilute solutions, magnesium limestones result, whilst with concentrated solutions normal dolomite is formed. Pfaff suggests that the dolomites of certain rock-masses may have been formed in a similar way in sea-basins when the salts have become concentrated.[54a] We may also note that a number of analyses of dolomite, magnesite, and of various ores have been published by the authorities of the Austrian Geological Survey.[55]

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[52] *Beiträge z. Mineralogie von Japan*, 1907, No. 3, 102.

[53] *Ibid.*, 104.

[54] *Abstr.*, 1907, ii, 480.

Eglestonite.—The small, cubic crystals from Terlingua have been analysed by Hillebrand.[56] The results establish the formula Hg_4Cl_2O, or $Hg_2O,2HgCl$, which must be accepted in preference to $Hg_6Cl_3O_2$, the formula given by Moses. Hydrochloric and nitric acids decompose the mineral with separation of calomel, but the hydrochloric acid filtrate contains no mercury, a fact in harmony with the view that the substance contains mercurous mercury only. It is at once blackened by ammonia.

Euxenite.—Brögger[57] has called attention to the close resemblance between euxenite and polycrase. The two minerals appear to belong to a series in which the ratio $(Cb,Ta)_2O_5 : TiO_2$ varies from 1 : 2 to 1 : 5. Brögger proposes to limit the name euxenite to those members in which the ratio is 1 : 3 or less, and to call polycrase those in which it is 1 : 4 or more. The ratio 1 : 3 was found in the case of a euxenite, from Alve, analysed by Blomstrand.

Evansite.—Specimens of this somewhat rare mineral from Goldburg, Idaho, and from near Columbiania, Alabama, have been examined by Schaller.[58] At the first of these localities, the massive, amorphous mineral occurs in seams. In colour, it is usually brown, but at times colourless, white, yellow, or dark red. The density varies with the colour and with the amount of iron present, from about 2·00 (6·6 per cent. Fe_2O_3) to 1·94 (2·15 per cent. Fe_2O_3). The index of refraction of the colourless variety is 1·485. Brown material gave the following results on analysis :

H_2O.	P_2O_5.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	Total.	Sp. gr.
36·96	19·14	5·49	34·48	4·32	trace	100·39	1·98

At the second locality, the mineral is found associated with coal. It is light brown and very brittle.

Fergusonite.—Brögger[59] has published an analysis by Blomstrand of fergusonite from Berg, in Råde, Norway. The crystals exhibit tetragonal symmetry, but under the microscope the material is seen to be amorphous, and this is probably due to alteration and hydration. A crystal when heated shows an incandescent glow and becomes fractured.

[54a] See also E. Phillipi, *Jahrb. Min.*, *Festband*, 1907, 397.

[55] *Jahrb. k. Geol. Reichsanstalt, Wien.*, 1907, **57**, 403.

[56] *Abstr.*, 1907, ii, 788.

[57] *Ibid.*, 885.

[58] *Ibid.*, 790.

[59] *Ibid.*, 884.

Glaserite.—In a paper on the formation and transformation of mixed crystals and double salts in the binary systems of the dimorphous sulphates of lithium, sodium, potassium, and silver, Nacken[60] has discussed the question of the individual existence of glaserite, $Na_2SO_4,3K_2SO_4$.[61] From a study of the freezing-point curves of mixtures of sodium and potassium sulphates, he concludes that glaserite exists as a hexagonal compound, $Na_2SO_4,3K_2SO_4$, at a temperature below the transformation temperatures of mixed crystals containing more or less Na_2SO_4 than itself. Glaserite does not mix with rhombic potassium sulphate, but forms with rhombic sodium sulphate a series of hexagonal mixed crystals of which the end member, *arcanite*, contains fifty-six molecular percentages of sodium sulphate at 181°.

Hamlinite.—In 1904, R. H. Solly described some honey-yellow, rhombohedral crystals from the Binnenthal, and believed them to represent a new species, which he termed *bowmanite.* The crystals he collected have since been examined by H. L. Bowman,[62] who has shown that in all probability they are to be referred to *hamlinite*, the basic strontium aluminium phosphate, $Al_3Sr(OH)_7P_2O_7$, described by S. L. Penfield.

Hussakite.—This name was assigned, in 1902, by J. Reitinger to a mineral from Dattas, near Diamantina, Brazil. The mineral closely resembled xenotime in its physical properties, but was found to contain a considerable quantity of SO_3. This result, which has led to the description of hussakite as an independent species in recent text-books, has been sharply criticised by E. Hussak,[63] who supplied the original material for analysis. After reviewing the evidence and supplementing it by fresh investigation, he concludes that hussakite is merely xenotime of prismatic habit and that it contains no SO_3, the supposed presence of this radicle being due to an analytical error. He therefore insists that the name hussakite should be abandoned.

Hutchinsonite.—The crystallography and optical characters of this very rare thallium mineral found in the Binnenthal by R. H. Solly have been carefully studied by G. F. H. Smith,[64] and the material has been examined chemically by Prior. The amount of substance available for analysis was unfortunately too small to admit of the composition being very accurately ascertained, but the results of two analyses, made on 0·018 gram and on 0·066 gram respectively, suggest the formula $(Tl,Ag,Cu)_2S,As_2S_3+PbS,As_2S_3$.

Ilmenorutile occurs in tetragonal crystals with the same habit as tapiolite and mossite. Brögger[65] regards it as an isomorphous mixture of $(TiO)TiO_3$ with $FeTiO_3$ and $Fe(CbO_3)_2$. Crystals from Evje and Tvedestrand respectively were found by O. N. Heidenreich to have the following composition :

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[60] *Jahrb. Min.*, 1907, *Beil.-Bd.*, **24**, 1.

[61] *Ann. Report*, 1906 319.

[62] *Abstr.*, 1907, ii, 703.

[63] *Centr. Min.*, 1907, 533.

[64] *Abstr.*, 1907, ii, 699.

[65] *Ibid.*, 884.

TiO_2.	SiO_2.	Cb_2O_5.	Ta_2O_5.	FeO.	MnO.	MgO.	CaO.
73·78	0·23	13·74	0·43	11·58	trace	0·04	0·22
67·68	0·05	20·31	—	11·68	trace	trace	0·28

Jamesonite.—An important contribution to our knowledge of this mineral has been made by L. J. Spencer,[66] who has measured a number of crystals from Cerro de Ubina, province Porco, Potosi, and finds the axial ratio $a:b=1:0·819$. The material examined by Spencer has been analysed by G. T. Prior, who obtained the following results: I, for crystals; II, for massive jamesonite.

	S.	Sb.	Pb.	Fe.	Cu.	Ag.	Total.	Sp. gr.
I.	20·52	34·53	41·18	2·76	0·26	0·01	99·26	5·519
II.	21·37	34·70	40·08	2·79	0·22	0·13	99·29	5·546

These numbers do not lead to any simple formula. They correspond fairly closely with $7(\frac{4}{5}Pb,\frac{1}{5}Fe)S,4Sb_2S_3$, which differs a good deal from the formula $2PbS,Sb_2S_3$ at present commonly accepted. Spencer, however, points out that the best analyses hitherto published are more in harmony with the complex formula than with the simple one given in the text-books.

Janosite.—The vexed question of the existence of a hydrated, normal ferric sulphate dimorphous with coquimbite, $Fe_2(SO_4)_3,9H_2O$,[67] has been the subject of a full discussion by Toborffy.[68] After calling attention to the agreement of the crystal-form, cleavage, and optical characters of janosite with those of copiapite, $2Fe_2O_3,5SO_3,18H_2O$, Toborffy points out that in attempting to establish new species in this group of minerals too much reliance must not be placed on small differences in the proportions of Fe_2O_3 and SO_3 present. These minerals are decomposition products and are exceedingly difficult to obtain pure, so much so that analyses of coquimbite and of copiapite by different chemists show wide divergences amongst themselves. In spite therefore of the fact that the composition of janosite agrees better with the formula $Fe_2O_3,3SO_3,9H_2O$ than with the formula $2Fe_2O_3,5SO$, $18\,_2O$, Toborffy comes to the conclusion that janosite is really identical with copiapite. In this view, he is in agreement with Weinschenk, but differs from him and from Linck in holding that copiapite is orthorhombic and not oblique.

Kleinite.—The remarkable mercury-ammonium mineral containing chlorine and SO_4, of which a preliminary account was given last year,[69] has been the subject of an exhaustive investigation by Hillebrand[70] and

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[66] *Abstr.*, 1907, ii, 700.

[67] *Ann. Report*, 1905, 279; 1906, 321.

[68] *Abstr.*, 1907, ii, 629.

[69] *Ann. Report*, 1906, 307.

[70] *Abstr.*, 1907, ii, 788.

Schaller. Their researches on this mineral and its associates, eglestonite, terlinguaite, and montroydite, will ultimately be described in detail in a special Bulletin of the United States Geological Survey; in the meantime, a condensed account has been published in the American Journal of Science. The material examined has proved to be identical with the unidentified mercury mineral No. 5 of Prof. Moses, and with the substance termed kleinite by A. Sachs, and this name is therefore accepted for it. The mineral occurs in hexagonal crystals with basal plane and pyramid faces, and has a good basal cleavage. In colour, it varies from canary-yellow to orange, and possesses the highly remarkable property of deepening in colour when exposed to light becoming paler again when kept in the dark. A basal section, instead of being isotropic, exhibits strong double refraction when viewed in polarised light, and is seen to have a highly composite structure. On heating above 130°, the birefringence diminishes and the section becomes uniaxial; it appears to revert very slowly to the biaxial condition on cooling. On heating above 130°, water is evolved, but no sublimate appears until the temperature is raised above 260°, when mercury and calomel are given off. During the sublimation of the calomel, a little chlorine appears to be evolved, and at a higher temperature more of this gas appears, followed later by another, apparently sulphur dioxide. Most of the nitrogen escapes as such during the sublimation of the calomel, and there is no evidence of the formation of ammonia. There is no certain evidence of the existence in the substance of hydrogen other than that present in water, or of oxygen other than that in water or in the SO_4 radicle. The average composition of orange-coloured crystals was as follows:

Hg.	Cl.	SO_4.	N.	H_2O.	Total.
85·86	7·30	3·10	2·57	1·03	99·86

The specimens analysed contained quantities of gangue ranging from 0·75 to 3 per cent. This was allowed for in calculating the average composition. The light-coloured crystals exhibited greater variations in, and slightly higher mean values for, the percentages of chlorine and SO_4 than did the darker ones. The presence of gangue increases the difficulties of the analysis, and gives rise to uncertainties, especially in the case of the water, the least satisfactorily determined constituent. No satisfactory formula can be calculated from the analytical results, which are neither in harmony with the formula $Hg[Cl\frac{1}{2}SO_4]_2[O(NH_2)_2]_3$, suggested by Sachs, nor with the assumption that the substance is a compound of the type NHg_2X,xH_2O, where X is Cl and SO_4. It seems possible that the mineral is a mixture.

Lautite.—An interesting find of this rare mineral has been reported by L. Dürr[71] from the mine "Gabe Gottes" in the Rauenthal, near Markirch, Alsace. The mineral, which somewhat resembles enargite in appearance, occurs in poor crystals, exhibiting three cleavages, *a* very good, *b* good, *c* poor. From measurements of the angles between these faces, it is concluded that the mineral is probably oblique. The following analysis agrees well with the composition $CuAsS$:

Cu.	As.	S.	Total.	Sp. gr.
37·07	44·53	18·30	99·90	4·53

This find resolves any doubts as to existence of the species *lautite*, originally named by A. Frenzel, in 1880, and later suspected of being a mixture.

Lengenbachite.—Thin foliæ of this mineral, found by R. H. Solly in the Binnenthal, have been analysed by A. Hutchinson,[72] who has found the following mean percentages:

Pb.	Ag.	Cu.	Fe.	As.	Sb.	S.	Total.	Sp. gr.
57·89	5·64	2·36	0·17	13·46	0·77	19·33	99·62	5·85

From these results, it is concluded that the mineral is of the type $7RS,2As_2S_3$, and that its formula is $6PbS(Ag,Cu)_2S,2As_2S_3$.

Magnetite.—Three specimens of crystallised titaniferous magnetite have been analysed by Harrington.[73] The first, from St. Joseph du Lac, Quebec (I), is remarkable for the high percentage of manganese present; the second, from Magnet Cove, Arkansas (II), is very rich in alumina and magnesia and is intermediate in composition between magnetite and spinel; the third, from Digby, Nova Scotia (III), corresponds to the formula Fe_3O_4, a little of the ferrous iron being replaced by magnesium. In each case, the ratio metals to oxygen is the normal one. The titanium may be regarded as present as Ti_2O_3, or as $FeTiO_3$, isomorphously replacing R_2O_3:

	Fe_2O_3.	TiO_2.	Al_2O_3.	FeO.	MnO.	MgO.	SiO_2.	Total.	Sp. gr.
I.	59·71	5·32	0·62	22·70	8·46	3·24	0·16	100·21	4·913
II.	59·01	2·40	10·37	16·82	2·10	9·47	—	100·17	4·558
III.	70·64	0·24	—	26·13	trace	2·97	0·03	100·01	5·067

Manganotantalite.—W. T. Schaller[74] has described small crystals from Mount Apatite, in Maine. Partial analysis proved the mineral to be almost pure columbo-tantalate of manganese, only 0·16 per cent. of ferrous oxide being present. The density is 7·14, a value which indicates that tantalic acid largely predominates over columbic acid.

Miargyrite.—L. J. Spencer[75] has found that the composition of a specimen from the Consuelo Lode, Tatasi, Potosi, can be represented as $8AgSbS_2 + CuSbS_2$.

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[71] *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1907, **6**, 249.

[72] *Abstr.*, 1907, ii, 277.

[73] *Ibid.*, 701.

[74] *Ibid.*, 790.

[75] *Ibid.*, 700.

Mica Group.—Tschermak's theory of the biotites has been discussed by Dalmer,[76] who comes to the conclusion that biotites are composed of mixtures of muscovite, $R_2Al_2Si_2O_8$, or phengite, $R_2Al_2Si_3O_{10}$, with olivine, $(Mg,Fe)_2SiO_4$. The proportions in which the constituents are mixed varies within the limits of 1 muscovite or phengite to 3 olivine, and 3 muscovite or phengite to 1 olivine. R_2 in the muscovite and phengite formulæ represent hydrogen and potassium, but these elements may be replaced by magnesium and ferrous iron, giving rise to compounds $(Mg,Fe)Al_2Si_2O_8$ and $(Mg,Fe)Al_2Si_3O_{10}$. Potassium is the predominant alkali metal; sodium occurs in small quantities only; lithium, in appreciable quantities, is only found in zinnwaldite and protolithionite. Silicic acid may be partially replaced by titanic acid, aluminium wholly or partially by tervalent iron. The olivine molecules are often partially or wholly hydrated. Calcium and manganese may occur, and traces of barium can be detected in many rock-forming biotites. In a number of biotites, especially in zinnwaldite, a part of the oxygen is replaced by fluorine. As regards special members of the group, we may note that Schaller[77] has deduced the metasilicate formula

$$(SiO_3)_{12}(AlF_2)_{4\cdot27}K_{4\cdot06}Li_{3\cdot84}Fe''_{1\cdot72}(AlO)_{0\cdot68}Al'''_{2\cdot57}$$

for a zinnwaldite from the York region of Alaska, and that a mica which occurs associated with lawsonite in Marin County, California, and which was described as margarite, has been found by Eakle[78] to be muscovite.

Molybdite (Molybdic Ochre).—The mineral of this name hitherto believed to be molybdenum trioxide, MoO_3, has been shown by Schaller[79] to be in reality a hydrated ferric molybdate, $Fe_2O_3,3MoO_3,7\frac{1}{2}H_2O$. This formula has been established by analysis of very pure material from Westmoreland, New Hampshire, and confirmed by examination of four other specimens: one from Telluride, Colorado; another from Renfrew, Ontario; a third probably of Californian origin, and a fourth from Hortense, Colorado. The New Hampshire mineral has a fibrous structure. The fibres give parallel extinction, and exhibit very strong pleochroism and absorption. Crystals of MoO_3 prepared artificially are quite different in appearance. Results very similar to these have since been obtained by F. N. Guild,[80] who has analysed a specimen from the Santa Rita Mountain, near the city of Tucson, and has arrived at the formula $Fe_2O_3,3MoO_3,7H_2O$. On the other hand, Prince G. Gagarine[81] believes that he has found pure molybdic oxide as white or grey pseudomorphs after molybdenite on specimens from the Ilmen Mountains.

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[76] *Abstr.*, 1907, ii, 183.

[77] *Ibid.*, 790.

[78] *Ibid.*, 484.

[79] *Ibid*, 480, 971.

[80] *Ibid.*, 629.

[81] *Ibid.*, 704.

Montroydite.—A large number of new forms have been determined on this orthorhombic mineral by Schaller.[82] A direct determination of oxygen as well as of mercury, made by Hillebrand, confirms the formula HgO.

Nepheline.—The formula $(K,Na)_2O,Al_2O_3,2SiO_2$ has been given by von Fedoroff[83] to material from the nepheline beds of the Turjin Peninsula.

Olivine.—An analysis by Schaller of an olivine occurring in a vein in the serpentine of Chester and Middlefield, Massachusetts, has been published by C. Palache,[84] who also gives reasons for regarding the so-called "hampshirite" of this neighbourhood as serpentine pseudomorphous after olivine, and not after humite, as suggested by A. L. Parsons.

Patronite.—Last year reference was made to a remarkable find of vanadium in Peru.[85] The mode of occurrence and composition of this deposit has recently been described in detail by Hillebrand.[86] The vanadiferous minerals occur in vein formation. Under the hanging wall is a thickness of about 8 feet of ore, an amorphous material of complex mineral composition, the principal constituent being patronite. Adjoining this is a hard, coke-like substance (86·6 per cent. of carbon), 8 inches to 2 feet in thickness, which merges into, and has possibly originated from, a lustrous, black material like asphaltite, for which the name quisqueite has been proposed (see p. 287). Hydrated oxidation products, rich in vanadium, ferric oxide, and silica, cover the ground in the vicinity of the outcrop. A bulk analysis of the ore showed it to consist in the main of sulphur (51·79 per cent.) and of vanadium (19·53 per cent.), together with iron, nickel, carbon, silica, and small quantities of other constituents. The ore yields sulphur when treated with carbon disulphide, and from the residue hot water extracts vanadium sulphate. In order to determine the composition of the patronite, the vanadium sulphide was removed by warm caustic soda from the material, which had already been extracted by carbon disulphide and water, and the proportions of vanadium and of sulphur in the solution were determined. The results indicate the formula VS_4 for the mineral, but it is possible that the free sulphur extracted by carbon disulphide may originally have been present combined with the vanadium. This view receives support from the fact that the proportion of free sulphur found increases with the length of time the mineral has been exposed to the air, indicating a progressive oxidation of the vanadium sulphide and liberation of sulphur. The iron and nickel present in the ore were found to be associated together as nickeliferous pyrites of the formula $(Fe,Ni)S_2$. The amount of nickel is so much greater than anything hitherto observed in pyrites that the specific name *bravoite* is suggested for this variety.

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[82] *Abstr.*, 1907, ii, 788.

[83] *Ibid.*, 562. See also J. Morozewicg, *Bull. Acad. Sci. Cracow*, 1907, 958.

[84] *Amer. J. Sci.*, 1907, [iv], **24**, 491.

[85] *Ann. Report*, 1906, 310.

[86] *Abstr.*, 1907, ii, 789.

Pilolite.—G. Friedel[87] has identified specimens of a kind of "mountain cork" found at Can Pey, near Arles-sur-Tech, Eastern Pyrennes, with a substance from Miramont, Haute-Loire, previously described by him under the name *lassallite.* The water-content and the composition of the residue after ignition have been determined for both varieties, and the formula $5SiO_2,Al_2O_3,MgO,3\frac{1}{2}H_2O$ suggested, which differs somewhat from that previously assigned to lassallite. As these minerals resemble closely those described by Heddle as pilolite, it is proposed to abandon the name lassallite.

Powellite.—Two specimens of this mineral, one from Llano Co., Texas, the other from Nye Co., Nevada, have been analysed by Schaller.[88] In both cases, the mineral is pseudomorphous after molybdenite, and the results, when impurities are allowed for, agree with the formula $CaMoO_4$.

Purpurite.—The discovery of this mineral at two new localities, Hill City, South Dakota, and Branchville, Connecticut, has enabled Schaller[89] to confirm the formula $2(Fe,Mn)PO_4,H_2O$ originally proposed for the mineral, and to establish the correctness of the view that the manganese and iron phosphates are present in isomorphous mixture. This is shown by the fact that in the original mineral from South Carolina manganese predominates, in that from South Dakota iron predominates, whilst in the Connecticut mineral iron and manganese are present in about equal amounts. The density of the South Dakota mineral was found to be 3·40, the value previously given, namely, 3·15, is too low. It shows straight extinction and strong pleochroism, rose-red parallel to the cleavage lines and bluish-purple perpendicular thereto.

Pyrites.—E. H. Kraus and T. D. Scott[90] have analysed and made exhaustive crystallographic determinations of the beautifully developed crystals of iron pyrites found at I, Central City Mine, Gilpin Co., Colorado; II, Franklin Furnace, New Jersey; III, an unknown locality in Colorado. The results are as follows:

	I.	II*a*.	II*b*.	III*a*.	III*b*.
Fe	46·51	45·12	45·28	46·31	46·39
S	53·26	53·34	53·26	53·06	53·11
Co	—	1·19	1·30	—	—
Ca	—	trace	—	—	—
Residue	0·59	0·02	0·03	0·54	0·52
Total	100·36	99·67	99·87	99·91	100·02

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[87] *Bull. Soc. franç. Min.*, 1907, **30**, 80.

[88] *Abstr.*, 1907, ii, 971.

[89] *Ibid.*, 790.

[90] *Zeitsch. Kryst. Min.*, 1907, **44**, 144.

These numbers agree very well with the accepted formula FeS_2. Nickel, cobalt, arsenic, antimony, and gold were looked for in I, but could not be detected.

Pyroxene Group.—It has long been known that the members of this family of minerals can be divided according to their chemical composition into three main groups. The first of these includes substances which may be regarded as members of a series of isomorphous mixtures, the end terms being diopside, $CaMgSi_2O_6$, and hedenbergite respectively, and for them in consequence $MgO + FeO = CaO$. The second, or augite group, comprises minerals which contain considerable quantities of alumina and ferric oxide, and these are regarded as mixtures of the diopside molecule $CaMgSi_2O_6$ with a molecule $Mg(Al,Fe)_2SiO_6$. In the third or aegirine-acmite group, alkalis play an important part, and $NaFeSi_2O_6$ is the predominant molecule. In the thirty-five years which have elapsed since this classification was proposed by Tschermak, advances in our knowledge have necessitated modifications in our views. Thus Wülfing has pointed out that most members of the diopside-hedenbergite series contain more MgO and FeO than can be accounted for by Tschermak's theory, and has suggested that in them an additional molecule, $MgFeSi_2O_6$, is present. Further, a number of pyroxenes have been discovered which contain still less calcium and more magnesium and iron than any hitherto admitted to the diopside-hedenbergite series, such, for example, are the pyroxene of the whin sill analysed by Teall, the pyroxene of a diabase from Richmond, S. Africa, examined by Cohen, and the pyroxenes which occur in the Juvinas, Shergotty, Nowo-Urei, and Busti meteorites.

This class of pyroxenes has lately formed the subject of an exhaustive review by W. Wahl,[91] who has brought together a large number of analysis, some thirty in all, and has made a careful study of two new examples. He has also examined the optical characters of many of the specimens, of which analyses have been published by other workers. He finds that these pyroxenes occur chiefly in diabases and in meteorites. They crystallise in the monoclinic system, contain little calcium, but are rich in magnesium and iron, the former of these two elements predominating in some specimens, and the latter in others. Many, especially those found in meteorites, show polysynthetic twinning parallel to 001. Optically, they are characterised by the abnormally low value of the optic axial angle, 2E, which is always smaller than in the case of members of the diopside series, and sometimes sinks to 0°. He finds, moreover, that the angle 2E may vary in different crystals from the same locality, or even in different portions of the same crystal. In this case, continuous variation is frequently met with, the angle increasing from the centre to the periphery. The extinction angle on 010 is lower than that of the diopside series.

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[91] *Tsch. Min. Mitt.*, 1907, **26**, 1.

Two characteristic examples have been analysed by Wahl.[91a] In the first, from Källsholm, Föglö, Alands Islands (analysis I, below), 2E reaches a maximum of 35° in the exterior portion of the crystalline grains, the centres being nearly uniaxial. The double refraction is fairly strong and positive; the extinction angle on 010 is 44½°. In the second, which occurs in a coarse-grained diabase near the village of Schtscheliki, on the S.W. bank of Lake Onega (analysis II, below), the angle 2E varies from about 41° in the interior to 73° on the outside; the extinction is 45°. In this, as in the majority of specimens examined, the plane of the optic axes is parallel to the plane of symmetry of the crystal:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	NiO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O	Total.
I.	51·30	0·72	2·36	2·22	18·83	0·05	0·57	16·56	6·96	0·21	0·37	1·00	101·15
II.	50·36	0·80	2·49	2·35	18·15	0·04	0·56	11·37	13·97	0·26	0·19	0·55	101·09

The optical characters of a pyroxene from the diabase of Richmond, Cape Colony, are, however, peculiar, inasmuch as when traversed across the field of the polariscope the value of 2E sinks from 31½° to 0° and then increases again to 20½° in a plane at right angles, the crystal remaining positive. That is to say, that, whilst the acute bisectrix maintains the same direction, the plane of the optic axes changes from a position parallel to the plane of symmetry to a position at right angles thereto. In the first position, the dispersion is $\rho > v$, and in the second $\rho < v$. The optic axis plane tends in fact to approach the position it occupies in enstatite and hypersthene if these substances are placed with their prismatic cleavage planes parallel to those of pyroxene. The pyroxene of the Juvinas meteorite exhibits similar behaviour.

These observations give the clue to the explanation suggested by Wahl, who points out that the composition and optical properties of these pyroxenes may be satisfactorily accounted for if we assume that in them we have a series of mixed crystals formed, on the one hand, by members of the diopside-hedenbergite (or augite) series and, on the other, by magnesium and iron metasilicates which have the optical properties of the rhombic pyroxenes. As the proportion of the latter increases, the percentage of calcium, the value of 2E, and the extinction angle diminish. This substitution may continue until the resulting mineral becomes uniaxial, or even until the optic axes separate again in a plane at right angles to the plane of symmetry. Wahl does not, however, think that the series is necessarily a continuous one, and he believes that probably a gap occurs, the series belonging to type IV or, perhaps, to type V of Roozeboom's classification. This explanation involves the crystallisation of monoclinic substances with rhombic ones. Any objection on this score is, however, more apparent than real, for the cleavages and angles are very similar in both classes of pyroxenes; indeed the rhombic members of the family have been sometimes held to be pseudorhombic and really monoclinic. Wahl therefore proposes that the name enstatite-augites should be assigned to these minerals. It should, however, be noticed that the magnesium metasilicate prepared artificially by Ebelmen has properties very similar to those of the pyroxenes of meteorites, and we may perhaps have to look to this substance rather than to enstatite or hypersthene for the other component of the mixed crystals. Wahl puts this view on one side, but the recent work of Allen, Wright, and Clement lends it probability, and further observations, especially synthetic experiments, are needed really to settle the question.

[91a] Compare also an analysis recently published by Dittrich of a pyroxene from Tasmania. *Centr. Min.*, 1907, 705.

Analyses of *hedenbergite* of *salite* and of other members of the pyroxene group have also been published by A. Rhein[92] and by N. Fukuchi.[93]

Pyrrhotite.—Four specimens of Sardinian pyrrhotites have been analysed by Serra.[94] One of them appears to have the formula FeS, but the remainder agree better with $Fe_{11}S_{12}$.

Rammelsbergite.—The following composition has been found by L. Dürr[95] for spherules with radial structure and silver-white, metallic lustre which occur at the mine "Gabe Gottes," Markirch, Alsace:

As.	Fe.	Ni.	Co.	S.	Total.	Sp. gr.
66·84	19·48	11·09	1·72	0·56	99·69	7·5

If the sulphur is assumed to be due to the presence of mispickel as an impurity, these results give the formula $Fe_{11}Ni_6CoAs_{31}$. This differs so widely from the type RAs, that Dürr thinks that the substance is possibly a mixture. The mineral resembles in composition chloanthite, from St. Andreasberg and so-called chathamite.

Rock Salt.—Stĕrba[96] has observed that the gases produced when blue rock-salt is dissolved in water always contain more hydrogen than the gases from colourless material. This observation appears to support the view that the blue colour is caused by sodium.

Samarskite.—Two new analyses have been published by Brögger,[97] but on optical examination the material was found to be not quite homogeneous, and no definite formula can be deduced from the results.

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[92] *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1907, **6**, 132.

[93] *Beiträge z. Mineralogie von Japan*, 1907, No. 3, 77, 83, 86, 92.

[94] *Abstr.*, 1907, ii, 361.

[95] *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1907, **6**, 230.

[96] *Anzeiger K. Akad. Wiss. Wien.*, 1907, 71.

[97] *Abstr.*, 1907, ii, 886.

Scheelite.—Lovisato[98] has described an occurrence of this mineral from Genna Gurèu, Sardinia. An analysis by C. Rimatori showed that it was exceedingly pure, the analytical numbers agreeing very closely with those required for the formula $CaWO_4$. Molybdenum, a constituent of all scheelites previously examined, was absent. The mineral was accompanied by meymacite (hydrated tungstic oxide), which was also submitted to analysis.

Selenium.—Minute flakes of selenium have been noted by R. Bellini[99] on lava of the Vesuvian eruption of 1906. This is interesting because it is doubtful whether selenium has ever hitherto been found native.

Semseyite.—An analysis by Prior of a specimen of semseyite containing silver has been published by L. J. Spencer.[1]

Smithite.—The composition of this rare mineral, found in the Binnenthal, has been ascertained by Prior to be as follows:

Ag.	As.	Sb.	S.	Total.	Sp. gr.
43·9	28·9	0·4	26·0	99·2	4·88

These numbers agree closely with the formula $AgAsS_2$. The crystallographic and optical characters have been determined by G. F. H. Smith.[2]

Stolpenite.—An amorphous, pink mineral resembling bole occurs in clefts in a basalt quarry near Nordheim, Rhön, and has been examined by Fersmann.[3] On analysis, it proved to be a member of the montmorillonite group, resembling a mineral from Stolpen in Saxony.

Terlinguaite.—Measurements by Schaller[4] of the oblique crystals have established the existence of a very large number of forms, and complete analyses by Hillebrand confirm the accepted formula Hg_2ClO, or $HgO,HgCl$. The mineral is decomposed by hydrochloric and nitric acids with separation of calomel. The hydrochloric acid filtrate contains bivalent mercury. It is not blackened by ammonia.

Tetrahedrite.—L. Dürr[5] gives the following analysis of a crystal from Markirch, Alsace, and thinks his results are best expressed by the formula $4Cu_2S,Sb_2S_3 + Cu_2S,FeS,ZnS,As_2S_3$:

Cu.	Fe.	Zn.	As.	Sb.	S.	Total.
42·13	3·48	4·40	9·74	12·44	27·00	99·19

Titanite.—J. Bruckmoser[6] has studied the acids obtained by Tschermak's method[7] from harmotome and from titanite. From the latter, the acid, $H_2Ti_2O_5$, is obtained as well as a silicic acid, $H_2Si_2O_5$. He concludes therefore that the formula of titanite is $Si_2O_5Ca_2O_5Ti_2$. Harmotome gave an acid, $H_8Si_5O_{14}$.

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[98] *Abstr.*, 1907, ii, 482.
[99] *Centr. Min.*, 1907, 611.
[1] *Abstr.*, 1907, ii, 700.
[2] *Ibid.*, 699.
[3] *Ibid.*, 561.
[4] *Ibid.*, 788.
[5] *Mitt. Geol. Landesanstalt Elsass-Lothringen*, 1907, **6**, 205.
[6] *Anzeiger K. Akad. Wiss. Wien*, 1907, 476.
[7] *Ann. Report*, 1906, 303.

Topaz.—Perfectly transparent, wine-yellow crystals[8] from Colorado have been found by G. P. Tschernik to have the following composition :

SiO_2.	TiO_2.	Al_2O_3.	CaO.	F.
32·69	0·13	55·36	0·08	20·43

Tourmaline.—The two following analyses have been made : (I), by Schaller[9] on carefully selected material got by breaking up pale pink crystals from Elba ; (II), by Serra[10] on material from large, black crystals found in a pegmatite vein at Asinara, Sardinia :

	SiO_2.	TiO_2.	P_2O_5.	B_2O_3.	Al_2O_3.	Ti_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	H_2O.	F.	Total.	Sp. gr.
I.	37·89	—	—	10·28	43·85	0·04	0·11	0·11	0·07	—	—	2·43	1·66	3·47	0·10	100·01	3·04—3·05
II.	35·43	0·56	trace	9·72	37·29	—	5·65	0·89	1·10	4·60	0·64	2·27	—	1·50	0·12	99·77	3·08

In analysis I the ratios $SiO_2 : B_2O_3$: total H = 4 : 0·93 : 20·08 ; numbers in harmony with Penfield's theory.

Trechmannite.—Qualitative tests make it probable that this species is a sulpharsenite of silver, but enough material for a quantitative analysis is not yet available. The morphological characters of the small, rhombohedral crystals have been fully determined by G. F. H. Smith.[11]

Tschermigite.—Octahedral crystals with cube faces, found in brown coal at Nieder Georgenthal, near Brüx, have been identified by A. Sachs[12] with the somewhat rare ammonium alum, *tschermigite.* The mineral proved on analysis to be nearly pure, and is optically perfectly isotropic. A specimen of the same mineral from Schellenken, near Dux, Bohemia, was found by Cornu[13] to have a density 1·636 at 18° and to be isotropic.

Valentinite.—Pure crystals from Bolivia have been found by Prior[14] to possess the accepted formula Sb_2O_3.

Yttrocerite.—The formula $Ce_2F_6,2Y_2F_6,9CaF_2,2H_2O$ has been found by Tschernik[15] for violet-blue crystals from Colorado :

Ce_2O_3.	Y_2O_3.	CaO.	H_2O.	F.	Al_2O_3,SiO_2.	Sp. gr.
18·19	29·36	27·61	1·96	37·69	trace	4·307

Yttrotantalite is isomorphous with samarskite, tantalum predominating in the former mineral and columbium in the latter. Two analyses have lately been published by Brögger.[16]

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[8] *Abstr.*, 1907, ii, 362.

[9] *Ibid.*, 790.

[10] *Ibid.*, 1908, ii, 116.

[11] *Ibid.*, 1907, ii, 699.

[12] *Ibid.*, 791.

[13] *Centr. Min.*, 1907, 467.

[14] *Abstr.*, 1907, ii, 700.

[15] *Ibid.*, 362.

[16] *Ibid.*, 887.

Zeolite Group.—Analyses of *analcite*, *chabazite*, *mesolite*, *natrolite*, *scolecite*, *stilbite*, and *thomsonite*, from New South Wales, have been published by C. Anderson,[17] and K. Jimbō [18] has investigated specimens of *analcite*, *apophyllite*, *stilbite*, and *heulandite* from Japan. Two members of this family have also been carefully studied by E. Baschieri,[19] namely, *natrolite* and the variety of *laumontite* termed *caporcianite* by Savi. To a specimen of the former from Montecatini, Val di Cecina, he assigns the formula $Na_2Al_2Si_3O_{10},2H_2O$, whilst he finds that the latter is $CaAl_2Si_4O_{14},4H_2O$. The acid isolated from both these minerals by Tschermak's method appear to be orthosilicic acid.

Special Reactions of Minerals.

In 1904, it was shown by Suida that silicates containing acid hydroxyl groups became strongly coloured when treated with solutions of basic aniline dyes. Cornu [20] has examined specimens of serpentine muscovite, lepidolite, and sericite which had been stained by Suida with methylene-blue or with magenta, and finds that they exhibit pleochroism, the absorption scheme being independent of the dye used. He concludes that the process of staining is not to be regarded as a purely physical phenomenon, but that chemical change probably takes place. Gaubert,[21] however, has found that minerals which are stained by basic colours also take up acid dyes, whilst chrysotile and pilolite absorb methylene-blue even after they have been heated to redness, and his observations have led him to the conclusion that the process of absorption is a physical one.

Cornu [22] has continued his experiments on the acid and alkaline reactions of minerals to which reference was made last year,[23] and has tabulated the results obtained for silicates, carbonates, phosphates, arsenates, borates, and certain hydroxides.

Meteorites.

Farrington [24] has made a useful compilation of about 360 published analyses of 248 meteoric irons, and has tabulated them according to the structure of the irons. The average composition of the irons is approximately: Fe, 90; Ni, 9; Co, 0·9, and Cu, 0·02 per cent. Of individual meteorites examined during the year, the two following from North Carolina are of interest, both have been described by Merrill [25] and analysed by Tassin.

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[17] *Abstr.*, 1907, ii, 887.
[18] *Beiträge z. Mineralogie von Japan*, 1907, No. 3, 115.
[19] *Proc. Verb. Soc. Toscana Sci. Nat.*, March 3, 1907.
[20] *Tsch. Min. Mitt.*, 1907, **25**, 453.
[21] *Abstr.*, 1907, ii, 479.
[22] *Tsch. Min. Mitt.*, 1907, **25**, 489.
[23] *Ann. Report*, 1906, 330.
[24] *Abstr.*, 1907, ii. 706.
[25] *Ibid.*, 278, 484.

Hendersonville.—This meteoric stone was found in 1901, but probably fell about 1876. It is chondritic in structure, and consists of enstatite, a monoclinic pyroxene, and olivine with metallic particles. Its mineralogical composition calculated from analyses is: nickel-iron, 2·59; troilite, 4·43; schreibersite, 0·08; chromite, 0·80; olivine, 40·48, and pyroxenes, 51·62 per cent.

Rich Mountain.—This stone was seen to fall in 1903. From analyses of the metallic portion and of the soluble and insoluble silicates, the following mineralogical composition has been calculated: nickel-iron, 7·831; troilite, 3·89; schreibersite, 0·20; olivine, 46·99; insoluble silicates (enstatite, &c.), 40·67; magnetite, 0·15, and graphite, 0·015 per cent.

In conclusion, attention must be called to the elaborate investigation made by F. Rinne and H. E. Boeke[26] of the meteoric iron named El Inca found in 1903 in the Pampa de Tamarugal, Iquique, Peru.

A. HUTCHINSON.

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[26] *Jahrb. Min. Festband,* 1907, 227.

RADIOACTIVITY.

α-Rays.

Rutherford[1] has collected in tabular form the twenty-three substances then known giving α-rays on disintegration, together with their periods of half-transformation, the range of their α-particles in air, and the initial kinetic energy possessed by the various individual α-particles on expulsion. The initial velocities of all the α-particles known lie between 1·56 and 2·25, and the critical velocity below which they can no longer be detected is 0·82 ($\times 10^9$ cm. per sec.). The heating effect produced by radium is a measure of the kinetic energy of the α-particles expelled, and, since the latter is of the same order for the individual α-particles of the various radioactive substances, it is valid to assume that the latter generate heat approximately in proportion to their radioactivity. It is pointed out that the kinetic energy of the α-particle increases progressively as the period of the transformation of the substance decreases, indicating that the energy evolved during disintegration is a function of the stability of the atom, being least for the most stable atoms. There are only three exceptions to this general rule, namely, in the case of radium *C*, thorium *X*, and actinium *X*. If the rule held universally, the periods in the three cases quoted as exceptional should be in each case less than one minute. There is a possibility that this is really the case, for if the changes in question were double, and the α-particle expelled in the second change, which was very rapid, the changes would be extremely difficult to analyse experimentally, and the period of the α-ray change would appear to be that of the first change. An actual case of this is to be found in thorium *B* and *C*, discussed at length last year.[2] Further, entirely independent evidence on this point has since been obtained in the case of radium *C* (compare pp. 319 and 338). If the views in this paper are substantiated, they show that the independence of the rate of atomic disintegration on the quantity of internal energy liberated,[3] which in the past has seemed one of the most curious features of the new process, is apparent rather than real.

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[1] *Abstr.*, 1907, ii, 63.

[2] *Ann. Report*, 1906, 333, 342.

[3] *Ibid.*, 313.

It is now possible to return with profit to the discussion held over last year,[4] of the reason for Mme. Curie's early observation, that if the α-rays are absorbed by two screens of different metals the extent of the absorption depends on the order in which the two metals are traversed by the rays. Some new experiments of Bragg[5] have thrown the necessary light on this very complex phenomenon. Rutherford established the simple law,[6] by direct measurement of the change of velocity of the α-particle after successive passages through similar thicknesses of aluminium foil, that the actual diminution of kinetic energy suffered by the α-particle is the same for each thickness, whether at the beginning or end of its path, and is therefore independent of the velocity of the particle. Bragg makes it clear that this is not universally true, but is rather a somewhat special and peculiar property of aluminium. The heavier metals absorb the α-rays more strongly at the beginning than at the end of their path, that is, the loss of kinetic energy suffered decreases with decrease of velocity. The complete ionisation curve for the α-rays of radium was determined under conditions in which the rays passed always through a fixed distance of 1·5 cm. of air, and also through a thin screen of the metal under examination, before entering the ionisation chamber. In one disposition, the screen was placed directly over the top of the radium, so that the rays passed through metal first and air afterwards; in the other, 1·5 cm. away, so that the rays traversed air first, then metal. In the first case, the α-rays traversed the metal at a higher velocity than in the second. With an aluminium screen there was no appreciable difference between the two dispositions, whereas a gold screen possessed appreciably greater stopping power in the first disposition with the rays moving at the higher velocity than in the second.

Using two different screens, in one case aluminium and tin, in another aluminium and gold, the stopping power of the combination was found to be clearly greater when the rays first traversed the denser metal. He considers that this new property of the α-rays suffices to explain Mme. Curie's effect without the explanation of Kučera and Mašek that it is due to the scattering of the α-rays. In a further paper,[7] Bragg and Cooke describe a beautiful extension of their result to the case of gases. It seemed likely that the stopping power of the atoms in general would exhibit the effect the more strongly the greater their mass. For example, hydrogen should stop the faster moving particles relatively less than air if the slower moving particles are taken as the basis of comparison. Hydrogen itself could not be tried for experimental reasons, as the apparatus was not large enough, but methane was compared as accurately as possible with air. The pressure and temperature of the two gases were adjusted, so that the slower moving α-particle from radium itself had the same range, and was therefore stopped equally by the two gases. It was found that the faster moving particles of radium *C* were appreciably more stopped by air than by methane. In consequence, the four steps in the ionisation curve are better shown by methane than by any other gas, and, in particular, the separate portions due to the α-rays from radium *A* and the emanation, the ranges of which are very similar, were very clearly separated. The effects are small, and on the extreme limit of what is practicable by present methods. They do not therefore affect the general truth of the earlier generalisation that the stopping power is proportional to the square root of the atomic weight. It is not necessary to do more than refer to the other papers published on this subject.[8] Edgar Meyer maintains his original conclusion that the effect of transposing the two screens can be calculated from the absorption produced by each separately at varying distances from the source of rays, but it is to be noticed that instead of the absorption, like the ionisation, increasing with diminishng velocity of the α-particle, as he supposed, the converse is the case.

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[4] *Ann. Report*, 1906, 341.

[5] *Abstr.*, 1907, ii, 324.

[6] *Ann. Report*, 1906, 335.

[7] *Abstr.*, 1907, ii, 733.

E. P. Adams[9] has carried out a determination of the ionisation ranges of the α-rays of polonium in eighteen different gases, which is of interest, as it includes many gases not previously examined. The polonium-coated plate floated on mercury in a tube, the top of which was closed by a glass plate covered on the inside with a film of zinc sulphide. The tube was filled with different gases at different pressures, and the extreme distance determined at which the scintillations could be seen when the plate was examined from above by a lens. The product of extreme distance into pressure was a constant for any one gas, and, for different gases, varied as the sum of the square roots of the constituent atoms in the molecule. Among the gases tried were nickel carbonyl, cyanogen, argon, and helium, and the latter are especially interesting as the result is an indirect confirmation of the accepted values for the atomic weights.[10]

Laby[11] has carried out a determination of the total ionisation produced by the α-rays of uranium in various gases by a method essentially different from that used by Bragg[12] for the α-rays of radium. Two identical ionisation vessels, each containing a similar plate coated with uranium oxide, and large enough to ensure complete absorption of the rays in the gas, were used, one being kept filled with air and serving as a standard of comparison, and the other containing the gas under investigation. The values obtained for the various gases are almost identical with those given by Bragg, showing that the total ionisation is independent of the nature of the α-ray employed, and confirming the result that the specific molecular ionisation is an additive property of the atoms in the molecule. This result has been extended by Kleeman[13] to the β- and γ-rays in an investigation of the ionisation in a large number of different gases with all three types of rays.

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[8] Kučera, *Abstr.*, 1907, ii, 219 ; Edgar Meyer, *ibid.*, 596 ; L. Meitner, *Physikal. Zeitsch.*, 1907, **8**, 489 ; Bragg, *ibid.*, 886.

[9] *Phys. Review*, 1907, **24**, 109.

[10] *Ann. Report*, 1906, 333.

[11] *Abstr.*, 1907, ii, 423.

[12] *Ann. Report*, 1906, 338.

The reputed α-radiation of uranium X[14] has now been more closely examined, and it appears very doubtful whether it can consist of α-rays. More probably it consists of expelled electrons of the kind which constitute the β- or δ-radiation. Hess[15] came to the conclusion, from a study of the absorption curves, that the rays were α-rays with a range of only 1 cm. in air, but the results of Levin[16] go against this view. From the absorption curves, he could find no evidence of α-rays, and by Bragg's method he obtained curves which he considered conclusively proved that there is no evidence of α-rays of greater range than 2 mm. of air. This evidence is, however, perhaps somewhat equivocal, as the ionisation shows an increase with increasing distance up to a maximum between 2 cm. and 4 cm. from the preparation. The best evidence seems to be the action of a magnetic field. Levin found that 34 per cent. of the total radiation consisted of the type under discussion, but, at most, only 10 per cent. of the total radiation could consist of non-penetrating rays, undeviable in a moderately strong magnetic field.

An experiment analogous to that of Logeman,[17] on a secondary electronic radiation, produced by impact of α-rays on matter, is described by Marcel Moulin.[18] The α-rays, freed from δ-rays by an electric field, passed through a gauze and impinged against a plate. The current with the plate positive to the gauze was much greater than with the plate negative to the gauze, for in the latter case the electrons expelled from the plate under bombardment of the α-particles do not escape from the plate.

E. Aschkinass[19] has found that a plate coated with polonium in a good vacuum, placed in a magnetic field arranged to return the δ-rays to their source, gains a negative charge. With no field acting it gains an equal and opposite positive charge, showing that the negative charge carried by the δ-rays exceeds the positive charge carried by the α-rays in the proportion of about two to one. According as the α-particle is supposed to carry one or two atomic charges, the number of δ-ray electrons emitted for every α-particle is either two or four. He regards his results as disproving the view that the α-particle, when initially expelled, is uncharged.

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[13] *Abstr.*, 1907, ii, 423.

[14] *Ann. Report*, 1906, 348.

[15] *Wien. Sitzungsber.*, 1907, 116, 109.

[16] *Abstr.*, 1907, ii, 220, 836.

[17] *Ann. Report*, 1906, 341.

[18] *Compt. rend.*, 1907, **144**, 1416.

[19] *Physikal. Zeitsch.*, 1907, **8**, 773.

Before leaving the subject of α-rays, the researches of J. J. Thomson[20] on the closely related positive rays (canal rays) in various gases in a vacuum tube may be briefly referred to. The ratio of the charge to the mass was measured by simultaneous electrostatic and magnetic deflection. In all gases except helium, this ratio assumed a value of either 10^4 or 5×10^3, whilst in helium, rays corresponding with $2{\cdot}5 \times 10^3$ were also observed. The value for the α-particle is 5×10^3, and if it is assumed that the charge is the single atomic charge, the mass in the three cases corresponds with the hydrogen atom, the hydrogen molecule or half the helium atom, and the helium atom. Stark has shown that helium is one of the few gases which can be made to give a line-spectrum under the action of the positive rays.

J. Kunz[21] has shown that the positive rays of the vacuum tube, like the α-rays to which they are analogous, cease to produce phosphorescence in willemite abruptly after passing through a definite distance of (highly rarefied) gas. The rays, however, have only about one-sixth of the velocity of the α-rays at their critical velocity when they cease to be effective in producing phosphorescence, and the great discrepancy between the two types has not been accounted for.

β, γ, and Secondary Rays.

There are, in general, two alternative ways of regarding the absorption of β-rays by matter. Either the β-particle, like the α-particle, may be regarded as pursuing its course through the atoms of matter subjected to a steady drain on its kinetic energy and velocity owing to its encounters with the atoms. Or it may possess the power of passing through the atoms of matter, for the most part completely unchecked until suddenly and completely stopped by some especially close encounter. The β-particle is an electron, and, compared with the massive α-particle, is very easily deviated from its course, so that on either view a considerable scattering of the primary beam during passage through matter is to be expected, and, in some cases, the apparent stoppage of a β-particle may be due to its being turned through a large arc, again to appear under the guise of "reflected," "scattered," or "secondary" radiation. The two views are not mutually exclusive, as both actions may, in fact, take place, but the important distinction between them is that on the first the diminution of the intensity of radiation in passage through matter is explained by an alteration in the individual energy, as well as in the number of the individual β-particles in the beam, whereas on the second view the effect is due to an alteration in the number only. The latter view, for which already there was some evidence,[22] has gained ground during the year.

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[20] *Phil. Mag.*, 1907, [vi], **13**, 561, and **14**, 295, 359.

[21] *Ibid.*, 1907, [vi], **14**, 614.

On this view, for a homogeneous β-radiation provided that the effects of scattering or reflection can be eliminated, since each successive element of thickness of the absorbing matter may be regarded as withdrawing the same definite fraction of the total number of β-particles, the absorption must follow an exponential law represented by

$$I = I_0 e^{-\lambda d},$$

where I_0 is the initial intensity, I the intensity after passage through a thickness d (cm.) of the material, and λ a numerical coefficient depending on the character of the radiation and the nature of the matter traversed.

H. W. Schmidt has investigated from this point of view the character of the β-radiation of radium E_2,[23] actinium B,[24] and uranium X.[25] The absorption of the β-radiation of radium E_2 by aluminium screens was found, for small thicknesses, to be nearly exponential, the absorption coefficient being about 40 (cm. $^{-1}$), so that one-half are absorbed in 0·173 mm. of aluminium. With greater thicknesses it increased considerably, the absorption becoming stronger as absorption proceeded. For other metals—lead, gold, and silver—the converse was found to be the case, the absorption coefficient decreasing with increasing thickness of material. This effect is ascribed to a far greater scattering of the rays in aluminium than in the denser metals. There results an effect precisely analogous to (but the converse of) that discussed under the α-rays, when two screens of different metals are employed. In this case the absorption is greater when the lighter metal is first traversed. β-Rays passing through an aluminium-lead screen are absorbed less than by a similar lead-aluminium screen. It is interesting to note here that, were this effect not due to scattering but to a true change in the absorption coefficients in the direction the measurements indicate, the two metals should absorb the more when the denser metal is first, as in the case of the α-rays.

Schmidt showed that a γ-radiation accompanied the β-radiation of radium E_2, but it is of very feeble intensity and penetrating power. The absorption coefficient for aluminium is 0·8 (cm. $^{-1}$), and the intensity only 0·016 per cent. of the β-rays. This is not in disagreement with the work of Stefan Meyer and E. von Schweidler,[26] who stated that no γ-rays exist greater than 0·03 per cent. of the β-rays.

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[22] *Ann. Report*, 1906, 349.

[23] *Abstr.*, 1907, ii, 520.

[24] *Physikal. Zeitsch.*, 1907, **8**, 737.

[25] *Ann. Physik*, 1907, **23**, 871.

A simple experiment showed that very considerable scattering of the primary beam of β-rays occurs in passage through a metal plate. The primary rays were cut down and confined to a narrow cone by means of metal stops, and the whole cone of rays received in the open end of an ionisation vessel. When the absorbing screen was placed directly over the open end of the latter a larger effect was obtained than when the screen was placed over the active preparation on the other side of the stops. It is probable that the deviations from the simple exponential law is due to this scattering, and a better approximation to the simple law ought to be obtained with a large flat surface of radiating substance than from a point source.

The velocity of the β-rays of radium E_2 was determined before and after passage through matter by the action of a magnetic field. It was found that no appreciable difference existed. The velocity found was $2{\cdot}49 \times 10^{10}$ cm. per sec., which is only 11 per cent. less than that found by Kaufmann for the fastest β-particles known—those emitted by radium C—which have an absorption coefficient for aluminium of only 13 (cm. $^{-1}$). Thus an eleven per cent. difference in velocity produces a change in the absorption coefficient of three times, and the comparatively slight change of absorption coefficient during absorption is additional evidence that the β-particle pursues its way through matter at an essentially constant speed, the absorption being primarily due to diminution in the number of β-particles in the beam by stoppage, reflection, and scattering. This is the exact converse of Bragg's conclusion for the α-particles.

In the work on the β-radiation of uranium X, a theoretical discussion of the effect of scattering or reflection of the primary beam leads to an analysis of the apparent absorption coefficient λ into two derived coefficients, one, α, representing the true absorption coefficient eliminating the effect of reflection, and the other, β, representing the reflection coefficient. When the fraction p of the total energy of the incident β-rays reflected back from a thick plate of material is known, $\alpha = \lambda \dfrac{1-p}{1+p}$ and $\beta = 2\lambda \dfrac{p}{1-p^2}$.

Two measurements of the intensity of the radiation after passage through the absorbing material, (1) with the active substance uncovered, and (2) covered with a thick plate of the absorbing material reflecting back the rays into the electroscope, suffice for the determination of λ and p, from which α and β may be calculated according to the admittedly somewhat imperfect analysis given. As McClelland had previously shown, the energy of the reflected radiation increases with the atomic weight of the substance acted on, except in the case of nickel (compare p. 320). With regard to the derived coefficients α and β, Schmidt finds that whereas these vary enormously for different metals, the reflection coefficient for gold being, for example, eighty times greater than for magnesium, they are connected with the atomic weight A and density D of the metal by the relations

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[26] *Ann. Report*, 1906, 352.

$$\beta/AD = 0{\cdot}124 \text{ and } \alpha/D\sqrt[3]{A} = 11{\cdot}2$$

with a maximum variation of only 14 per cent. Fourteen metals were examined. The expressions indicate that absorption is proportional to the sum of the cross-sections of the atoms contained in the absorbing material, while reflection is proportional to the mass of the atom and the volume it occupies. Levin[27] has also investigated the absorption curve of the β-rays of uranium X, and found that it departs noticeably from the exponential form. For the β-rays of actinium B, Schmidt found very similar relations to those described for uranium X.

McClelland and Hackett[28] have examined their earlier results from the point of view of the part played by "secondary radiation" on the absorption coefficient. It may be pointed out that they worked with the β-rays, presumably, of radium C, which, there is some evidence to believe, are composed of more than one type. They show that the true coefficient of absorption μ can be calculated from the apparent coefficient λ. If k represents the ratio of the energy of the secondary particles emitted from an element of volume to that of the particles absorbed in that element, $\mu = \frac{\lambda}{\sqrt{1-k}}$; μ divided by the density increases with the atomic weight, and the elements fall into periods with respect to this ratio, similar to the chemical periods.

Of the complexity of the process of absorption and the importance of eliminating the action of secondary or scattered radiation, there is thus no doubt, but the results of different investigators are not in complete agreement, and it will probably be some time before a complete theory can be given of the action.

A. S. Mackenzie[29] has examined the secondary radiation from a lead plate exposed to the β- and the γ-rays of radium, both from the surface directly exposed to the radium (reflected secondary rays) and from the back surface (transmitted secondary rays). He has analysed the secondary radiation into the separate parts due to the β- and γ-rays respectively. Whereas the intensity of the reflected secondary rays due to the β-rays does not further increase with the thickness of the reflecting plate after a thickness of 0·25 mm., the intensity of the transmitted secondary rays due to β-rays increases without limit with the thickness of the reflecting plate up to 15·6 mm. This is a result very difficult to account for.

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[27] *Abstr.*, 1907, ii, 836

[23] *Ibid.*, 420.

[29] *Ibid.*, 596.

R. T. Beatty[30] deals with the secondary Röntgen radiation produced from air, and J. A. Crowther[31] with that produced from a large number of gases and vapours. The latter finds that all gases and vapours subjected to the *X*-rays are a source of secondary radiation, and divides them into two classes, those which merely scatter the primary radiation, and those which transform the radiation, producing rays much more intense and of a softer character than in the first case. In the first class fall the elements with atomic weights below that of sulphur, for which, with the exception of hydrogen, the secondary radiation is proportional to the atomic weight, and, in the second class, the elements with atomic weight greater than sulphur.

Kleeman[32] examined the secondary cathode radiation emitted by various elements exposed to the action of the γ-rays, and describes a connexion between the amount of secondary radiation and the position of the element in the periodic table. He found that the γ-rays of radium fall into two groups. The first are more efficient in producing secondary radiation from aluminium, iron, nickel, zinc, and tin than from lead, and this secondary radiation is more easily absorbed by any of these substances than by lead. The second group produces secondary radiation more efficiently from lead than from any other substance, and the secondary radiation is more readily absorbed by lead, bismuth, and mercury than by other metals. Hence, to screen most efficiently from the γ-rays a screen of lead and copper or zinc would be more efficient than a similar thickness of lead alone. These two types of γ-rays may correspond with the two types of β-rays of different velocities known to exist in the radiation of radium *C* from the work of Paschen and Schmidt (compare also p. 311).

P. D. Innes[33] has examined the velocities of the electrons emitted as secondary radiation by metals under the influence of Röntgen radiation of varying intensity and hardness or penetrating power. The electrons expelled are not all of the same velocity, but vary over a certain range. In the case of lead, silver, zinc, platinum, and gold the velocity of the electrons was independent of the intensity of the primary radiation, but hard rays produced electrons of greater maximum velocity than soft rays. Whereas for all metals the minimum velocity of the expelled electrons is the same, about 6·2 ($\times 10^9$ cm. per sec.), the maximum velocity of the electrons was higher in the case of the metals of heavier atomic weight, ranging from 6·4 in the case of zinc to 7·5 in the case of platinum. The origin of the electrons, and the question whether they are derived from free electrons in the metal or are formed as the result of an "atomic disintegration," are discussed in favour of the latter view. The fact that the velocity is completely independent of the intensity of the primary radiation, and the variation of the velocity with different metals, are urged in favour of the view that their energy is derived from the internal energy of the atom, and not from the primary radiation. There appears, however, nothing in the arguments used which would not apply equally to chemically combined electrons, in which case the source of the energy would not be that which the radio-elements draw upon, but the ordinary chemical energy of the atom. The existence of chemical energy in matter seems to have been overlooked.[34]

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[30] *Phil. Mag.*, 1907, [vi], **14**, 604.

[31] *Abstr.*, 1907, ii, 922.

[32] *Ibid.*, 923.

[33] *Proc. Roy. Soc.*, 1907, **79**, *A*, 442.

J. J. Thomson[35] found that the secondary radiation given out by a plate of substance exposed to the X-rays increases invariably with the atomic weight of the element, with the single exception of nickel, for which an atomic weight greater than cobalt is indicated. The secondary radiation increases with atomic weight at a rate which is by no means uniform, and at places a large increase of secondary radiation accompanies a small increase in atomic weight. The secondary radiation in this case refers to the secondary emission of electrons, not to true secondary X-rays, and is very easily absorbed by gases.

Barkla and Sadler[36] examine in detail the question of the atomic weight of nickel as raised by their early experiments and those of others, experimenting with X-rays. Their work refers to the true secondary X-rays, not cathode-rays or expelled electrons. Such rays, produced by impact of X-rays on a metal plate, are especially penetrating to the same metal as that from which they are radiated.

The nearer the atomic weight of the absorbing metal to that of the radiating metal the less the absorption, and it is found by this test that cobalt is nearer to iron than to nickel, and nickel is nearest in atomic weight to copper. The atomic weight of a metal may be calculated with great exactness from its opacity to secondary X-rays, and nickel becomes quite normal in its behaviour with respect to the X-rays if an atomic weight of 61·4, between copper and cobalt, is assigned to it instead of 58·7.

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[34] Compare *Ann. Report*, 1905, 302.

[35] *Abstr.*, 1907, ii, 220.

[36] *Ibid.*, 731.

McClelland and Hackett[37] found nickel to be quite normal so far as its behaviour to the secondary radiation produced by the β-rays of radium C is concerned, but H. W. Schmidt[38] found it abnormal using the β-rays of uranium X, and less markedly so with the β-rays of actinium.

Bragg[39] advocates the view that the γ- and X-rays are, at least in part, due to the flight of a neutral particle composed of a pair of positive and negative electrons, and that they are therefore, like the β-rays, corpuscular rather than ethereal in nature.[40]

Helium and Ultimate Disintegration Products.

Sir James Dewar[41] suggests the use of the radiometer for observing small gas pressure and the detection of helium produced by radioactive bodies. Radiometers constructed with a side tube containing charcoal have been constructed with so good a vacuum that the vanes do not rotate even under the influence of the beam from an arc lamp concentrated by a lens on the vanes. If the non-condensible constituents of the atmosphere have been replaced during preliminary exhaustion by oxygen and nitrogen from the evaporation of liquid air, and no hydrogen is present, cessation of motion ensues after the charcoal has been immersed for some time, even in liquid air. Radiometers in which hydrogen is the residual gas, show no motion when liquid hydrogen is used to cool the charcoal, but if helium is the residual gas the vanes still move freely in these circumstances. A little radium bromide was placed in a side tube in a properly constructed radiometer of the kind described. At first, immersion of the charcoal in liquid air sufficed completely to stop the vanes, but after fifteen hours the radiometer became quite active, and now immersion of the charcoal in liquid hydrogen did not produce cessation of motion, indicating a production of helium by the radium.

Greinacher and Kernbaum[42] describe attempts to detect helium produced from polonium, which, so far, have given a negative result. K. A. Hofmann and Wölfl,[43] in their work on radioactive lead (see p. 337), remark incidentally that a preparation of radioactive lead sulphate sealed up in a completely exhausted capillary tube showed, after a period of several months, the three chief helium lines in the spectroscope, although all experiments with radium *E* and polonium have so far given absolutely no result. Giesel[44] sealed up half a gram of the oxide of a very active emanium (actinium) preparation in an exhausted Geissler tube. No alteration of the vacuum was noticed for more than two years, but latterly, after heating the substance, it has been possible to see the D_3 helium line in the spectrum. This confirms the previous observation of Debierne.[45]

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[37] *Nature*, 1907, 535.

[38] *Loc. cit.*

[39] *Phil. Mag.*, 1907, [vi], **14**, 429.

[40] See also Barkla, *Nature*, 1907, 66; Bragg, *ibid.*, 1908, 270.

[41] *Proc. Roy. Soc.*, 1907, **79**, *A*, 529.

[42] *Abstr.*, 1907, ii, 422.

[43] *Ibid.*, 521.

A possible source of error in experiments involving the spectroscopic detection of minute quantities of the rare gases appears from the work of F. Soddy and T. D. Mackenzie.[46] The gases evolved from a number of new spectrum tubes, provided with aluminium electrodes, during preliminary exhaustion and passage of the discharge, were absorbed by volatilising calcium. There remained a considerable quantity, from the spectroscopic standpoint, of pure helium. It was then found that aluminium electrodes, which have been used in spectrum tubes with the rare gases, tenaciously retain these gases, and give them up when remounted and used in a new spectrum tube. Helium, neon, and argon were each obtained from old aluminium electrodes, used at one time with these gases respectively, although after removal from their original spectrum tubes they had been kept for months exposed to the open air. That even new spectrum tubes, as obtained from the maker, cannot be implicitly trusted in this work is shown by the fact that the phenomenon was actually discovered with such tubes.

In a paper on the ultimate disintegration products of uranium, Boltwood[47] examines the published analyses of uranium minerals, and finds the ratio of lead to uranium varies in forty-three minerals from 0·04 to 0·25. Minerals from the same locality show very good agreement in this ratio. He cites an opinion of Prof. Joseph Barrell that the relative values of the ratio in the different groups corresponding to different localities "are not contradictory to the order of the ages attributed by geologists to the formations in which the different minerals occur." He proceeds: "on the basis of this evidence the assumption would appear to be justified that lead is the final product of uranium." Assuming the helium in the minerals to be formed according to the equation,

$$\text{Uranium } (238{\cdot}5) = \text{Lead } (206{\cdot}9) + \text{Helium } (31{\cdot}6),$$

the amount of helium corresponding with the amount of lead in the minerals is calculated. In no case is the amount found more than that calculated. The ratio of the found to the calculated varies from 100 per cent. in one case to 6 per cent. in another, the denser minerals usually retaining the greater proportion of the helium. The data on which the actual quantities of helium present in the minerals are based are extremely untrustworthy. The age of the minerals, on the assumption that the fraction of uranium transformed yearly is 10^{-10}, is worked out from the ratio of uranium to lead, and varies in the different groups from 410 to 2,200 million years. The relative proportions of uranium and thorium may show large variations in minerals without the ratio of uranium to lead being affected, and it is concluded with certainty that lead is not a product of thorium. Helium is regarded as probably not a product of thorium, for even in thorianite the amount of helium is only one-half of that produced by the uranium calculated from the ratio of lead to uranium on the assumptions given.

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[44] *Abstr.*, 1907, ii, 597.

[45] *Ann. Report*, 1905, 303.

[46] *Proc. Roy. Soc.*, 1908, **80**, *A*, 92.

[47] *Abstr.*, 1907, ii, 220.

Strutt[48] cites the case of a mineral resembling fluor-spar, but containing rare earths, from Ivitgut, Greenland, described by Julius Thomsen. He determined the helium, which is 0·027 c.c. per gram, and found a considerable quantity of thorium, but no radium, in the mineral. He considers it entirely certain that in this case the helium has not been generated by uranium or radium, and ascribes it to the thorium.

Szilard[49] points out that in uraninite the relative quantities of thorium and uranium are always within the same limits—4 to 11 per cent., and 65 to 74 per cent. respectively—as the relative quantities of uranium and thorium in thorianite. A body with the same uranium and thorium content as thorianite is obtained by dissolving thorium hydroxide in a solution of uranyl nitrate, and with the same metallic content as uraninite by dissolving uranyl hydroxide in a solution of thorium nitrate. Aqueous solutions of the salts of thorium and uranium possess the property of dissolving almost all the hydroxides of the rare earths and metals found in thorianite and uraninite. All these substances are amorphous when prepared in this way. Szilard suggests that the formation of the minerals thorianite and uraninite is due to the properties described.

Cady and McFarland[50] have examined forty-one sources of natural gas in America for helium, by Dewar's charcoal method, and found helium in all, varying from traces up to as much as 1·84 per cent. No less than four samples contained more than 1·5 per cent., and in these the nitrogen content varied from 50 to 80 per cent. It was found that the helium increased with the nitrogen, although not in any simple relation.

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[48] *Proc. Roy. Soc.*, 1908, **80**, *A*, 56.

[49] *Abstr.*, 1907, ii, 888.

[50] *Ibid.*, 949.

Thorium.

This element, which was the centre of much interesting and suggestive work last year,[51] again occupies a position of outstanding importance. It is of historical interest to note that the original observation of the chemical separation from, and the spontaneous generation of thorium *X* in, a thorium solution, led to the disintegration theory of radioactivity being put forward. During the present year, it has transpired that in this operation of separating thorium *X*, by precipitating the thorium as hydroxide with ammonia, another disintegration product, "mesothorium," intermediate between thorium *X* and thorium, is also separated, the existence of which, owing to the peculiar characteristics of the successive disintegrations, had previously not even been suspected. There are some grounds for the hope that in this extremely complicated series of changes something like finality has at last been reached.

It will be convenient, first, to consider the decay constant or period of radiothorium, the non-thorium substance exhibiting all the main features of the radioactivity of thorium in an intense degree, separated by Hahn from thorianite, and by Elster and Geitel, and G. A. Blanc from the sediments of certain hot springs[52] Hahn noticed a slow, gradual falling off of activity of his preparations, and obtained an idea of the order of magnitude of the decay constant, which was sufficiently near to lead him on to the discovery of mesothorium about to be considered. G. A. Blanc[53] has, however, accurately measured this constant, using a specimen of radiothorium, separated by Angelucci from the sediment of the hot spring at Echaillon. A nearly exponential diminution of activity with time during a period of several months, is recorded, corresponding with a period of half-transformation of 737 days, or almost exactly two years. This value is provisional until more extended observations can be performed.

O. Hahn[54] concluded from his own observation of the order of this period, that a new intermediate product must exist between thorium and radiothorium. It will be recalled[55] that certain thorium salts prepared by Boltwood directly from minerals, had a specific activity about twice as great as the commercial salts, prepared by processes for the most part unknown. This led to the conclusion that although no known laboratory process was effective in separating radiothorium from thorium, the secret processes used in commerce must separate one-half of the radiothorium. An examination of the residue obtained in the manufacture disproved this view. Hahn found no evidence of such separation in the products of a Berlin factory, nor did Boltwood [56] in the products of an American factory. On the other hand, the latter, investigating the rate of regeneration of radiothorium in preparations partly deprived of it, came to the conclusion that the period of radiothorium was not less than six years. To account for the discrepancy, Hahn examined the activity of a series of commercial thorium salts of different ages since preparation. He found that the newly-prepared commercial salts, like the laboratory-prepared salts of Boltwood, had a normal specific activity, and therefore possessed their full quota of radiothorium. With increasing age, the activity steadily diminishes, and reaches a minimum after about two years, at which it remains constant for some time, and then, for old preparations, gradually increases. The older the preparation the more nearly normal is its specific activity. This initial decay before recovery would occur if there existed a parent of radiothorium intermediate between it and thorium, absent in the freshly-prepared specimens, and gradually regenerated by the thorium with lapse of time. The effect, then, has nothing to do with the method of preparation of the thorium salt, but is purely a question of age. Hahn concluded that the period of this parent (mesothorium) is longer, but not incomparably longer, than that of radiothorium, and as a first approximation, estimated it at about seven years. The direct proof of the view was found in the separation of preparations, free from thorium, and possessing a *continuously increasing* α-activity, and also power of giving the thorium emanation, during a period of several months; this is mesothorium. Radiothorium, after the first month, when the amount of thorium X present attains equilibrium, shows no further increase of radioactivity, but rather a gradual decay.

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[51] *Ann. Report*, 1906, 360.

[52] *Ibid.*, 360.

[53] *Abstr.*, 1907, ii, 324.

[54] *Ibid.*, 359.

[55] *Ann. Report*, 1906, 362.

Boltwood obtained striking confirmation of this view. His own thorium preparations, originally of normal specific gravity, had in the meantime decayed, and the rate of decay from the known constant of radiothorium indicated that the greater part of the mesothorium had been separated in their preparation. One of the preparations, which had decayed in activity, had been prepared, by precipitation with ammonia, from a thorium nitrate which retained its original activity, showing that this process separates, not only thorium X, but also mesothorium. Although the separation of mesothorium from thorium and of thorium X from radiothorium is easily accomplished, there is no known method of separating by chemical means either radiothorium from thorium or thorium X from mesothorium. But owing to these last-mentioned pairs alternating in the disintegration series, each of them can readily be prepared by itself. For example, the preparations of radiothorium obtained by Hahn and others are probably not the radiothorium existing in the mineral at all, but regenerated radiothorium, subsequently produced after the separation, from the easily separated mesothorium. In a later paper, Hahn[57] concludes indirectly from observations of the radiations from different thorium preparations, that thorium itself gives out a true α-radiation in changing into mesothorium, whilst the latter gives out a β-radiation but no α-radiation. The disintegration series is now:

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[56] *Abstr.*, 1907, ii, 731.

Thorium (α-rays) $\longrightarrow$ mesothorium (β-rays) $\longrightarrow$ radiothorium (α-rays) $\longrightarrow$ thorium X (α-rays) $\longrightarrow$ emanation (α-rays) $\longrightarrow$ thorium A (δ-rays) $\longrightarrow$ thorium B and C (α-, β-, and γ-rays).

Hitherto it has been supposed that the 25 per cent. "non-separable α-activity" of thorium was due to radiothorium, and that the initial change of thorium was rayless. In a simultaneous study of the changes in α-ray activity and in emanating power of thorium preparations, it is found that the former varies less than the latter, indicating a constant α-radiation from the thorium itself. The β-rays do not change concomitantly with the emanating power, as they should if thorium B (and C) were the only source of β-rays, and it was found that mesothorium emits β-rays. The result of Levin,[58] that thorium B alone gives β-rays, is not affected, as his thorium preparations were not old enough to have contained mesothorium. One of Hahn's preparations emits relatively 100 times more β- than α-rays compared with thorium preparations themselves, and, of course, its α-activity may be expected to grow steadily with time over the next few decades until it becomes normal with respect to the β-activity.

G. Hoffmann,[59] continuing his researches on thorium X,[60] has applied Nernst's theory of the connexion between ionic mobility and diffusion constant to a determination of the valency of thorium X. An electrolyte diffusing, not into pure water, but into a uniform solution of another electrolyte containing a common anion, shows a diffusion velocity more and more nearly approaching that corresponding to the mobility of the cation alone as the ratio of the concentration of the diffusing electrolyte to the other electrolyte becomes infinitesimal. This condition is fulfilled in the diffusion of the cation, thorium X, in a solution of an electrolyte. The coefficient of diffusion of thorium X, as previously determined, is 0·504 cm.^{2}/day at 10°. In the present paper, the ionic mobility of thorium *X* is determined by electrolysis, carried out between electrodes of copper in a tube bent into a large number of double U's, in a solution of uniform concentration of copper sulphate or ammonium nitrate. The thorium *X* is confined to the electrolyte in the central U, and during electrolysis migrates into the U nearer the cathode, but not appreciably to the anode. The concentration of thorium *X* in (1) the unelectrolysed solution, part of which is put into the central U for the electrolysis; (2) the solution remaining in the central U after electrolysis; (3) the solution in the U nearer the cathode after electrolysis, gives the velocity of migration of the thorium *X* ion under the observed potential gradient in the usual way. The measurement of these three concentrations was carried out, after the electrolysis, by placing similar volumes of the three liquids, at the same time, in three similar vessels in which the active deposit from the thorium emanation is collected on a negatively charged plate for a period of twelve hours. Under these conditions the decay of the thorium *X* need not be taken into account, and the activity of the plate remains constant, after removal from the emanation, for a sufficient period to allow of its measurement. The value found for the ionic mobility in ten electrolyses was between 0·8 and 1·2 cm. per hour under unit potential gradient of 1 volt per cm. at 18°, and the lower value is the more likely to be correct. The value calculated from Nernst's theory from the diffusion coefficient is 1·03 at 18°, on the assumption that the thorium *X* ion carries a single charge, and is therefore monovalent. The agreement between the found and calculated values is thus evidence that thorium *X* is a univalent substance. This research forms a notable example of the application of electrochemical methods to the infinitesimal quantities of matter dealt with in radioactivity.

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[57] *Abstr.*, 1907, ii, 664.

[58] *Ann. Report*, 1906, 348.

[59] *Physikal. Zeitsch.*, 1907, **8**, 553.

[60] *Ann. Report*, 1906, 363.

Angelucci,[61] by the electrolysis of thorium nitrate solutions, has separated on the cathode pure thorium *A*. On the anode, an oxide is deposited containing thorium *X*.

Actinium.

O. Hahn[62] describes in detail the properties of the new product radioactinium. The period of half-transformation is given as 19·5 days, instead of 20 days, as in earlier communications. If an actinium preparation is precipitated repeatedly with ammonia, the actinium *X*, but not the radioactinium, is removed, and the emanating power falls practically to zero. The actinium retains, however, from 22 to 25 per cent. of its initial α-activity. When the

[61] *Abstr.*, 1907, ii, 773.

[62] *Ibid.*, 62.

radioactinium also is precipitated, for example, with amorphous sulphur, by adding sodium thiosulphate to the acid solution, the α-ray activity falls to a very low value, and there is every reason to believe that actinium, if perfectly freed from its products, would be completely inactive. Radioactinium is not volatilised at the temperature of the ordinary blowpipe, whereas actinium *A* and *B* are freely volatile. No definite chemical nature can be assigned to the substance. Levin [63] has made some observations in this connexion. Giesel [64] explains many of his earlier observations with actinium (emanium) in the light of Hahn's discovery of radioactinium, and ascribes to the latter body a chemical nature analogous to the alkali earth metals, as it is readily precipitated by sulphuric acid at least in the presence of strontium and barium. It may be that the use of finely-divided sulphur in its separation depends on the formation of a trace of sulphuric acid. In investigating a very strong preparation of actinium prepared some years previously, the presence of a new emanation, showing characteristic properties, was observed. When introduced into the electroscope, the gas did not show the initial increase in activity characteristic of radium emanation. On the contrary, a much slower increase occurred, the activity reaching a value double the initial in from two to three days, and then remaining constant for two or three weeks. On exposing the apparatus to air, the leakage became normal in a few hours, showing that no long-lived active deposit was produced. Levin,[65] using three grams of an actinium preparation prepared by Giesel, did not succeed in obtaining this result. The gas after the decay of the actinium emanation showed all the characteristics of radium emanation.

Debierne [66] has investigated the diffusion coefficient of the actinium emanation by measuring the distribution of intensity of the active deposit on a vertical plate fixed at right angles above an actinium preparation. His value indicates an atomic weight of only 70 (?) for the emanation, but it appears uncertain whether the theory of diffusion can be applied correctly to the case of the radioactive emanation.[67]

St. Meyer and E. von Schweidler [68] have investigated the small residual activity of the active deposit from actinium,[69] and confirmed their first results. The decay is only approximately exponential, and the period is 11·8 days. The substance is not appreciably volatilised at a bright red heat, and itself produces no induced activity on bodies in its neighbourhood. These two properties negative the otherwise plausible view that it may be caused by volatilisation of some actinium X or radioactinium from actinium at the ordinary temperature. That it is due to a direct further disintegration of actinium B into actinium C, &c., is only possible if the radiation has an extremely low penetrating and ionising power, for the activity, although it is extremely feeble, decays rapidly. Since the period is only twelve days, equilibrium should be rapidly attained, and the intensity of the radioactivity should be the same as that of the actinium B initially present, if it results directly from it, and the rays emitted are of average intensity. The radiation is certainly of the easily absorbed type, but is too feeble for exact investigation. The ratio of the intensity of the initial activity of the active deposit to the residual activity, which, after long exposure to the actinum, should be a constant on the view discussed, is only roughly so, and varied in six experiments from 4 to $0{\cdot}4 \times 10^4$. The possibility is not excluded that the phenomenon is not due to actinium at all, but to another radioactive substance present with it (compare p. 331). It is one of the most interesting radioactive phenomena at the present time.

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[63] *Physikal. Zeitsch.*, 1907, **8**, 132.

[64] *Abstr.*, 1907, ii, 597.

[65] *Ibid.*, 922.

[66] *Le Radium*, June, 1907.

[67] Only an abstract of this paper is available to the writer.

[68] *Wien. Sitzungsber.*, 1907, 116, IIA.

[69] *Ann. Report*, 1906, 363.

V. F. Hess[70] has determined the period of actinium A, in numerous experiments, with three separate actinium preparations. He found the decay to be strictly exponential, and the mean period was 36·7 minutes. No great variation in this value was noticed in any circumstances, and it is possible that the very varying values obtained by earlier observers may be due to other radioactive substances present with the actinium.

Parent of Radium.

Early experiments[71] have shown both that uranium must be the first parent of radium, since the ratio of uranium to radium is constant in all minerals, and that uranium initially freed from radium does not generate radium at a rate greater than one-thousandth part of what is to be expected if a direct transformation took place. Experiments have been continued by F. Soddy and T. D. Mackenzie,[72] in which methods of purification of the uranium, depending on the solubility of uranyl nitrate in ether, have been used with the object of removing not only radium, but also the intermediate products between uranium and radium, the existence of which followed from the earlier results. Several quantities of uranyl nitrate, each containing several hundred grams of uranium, have been purified and tested periodically for the presence of radium, in one case during 600 days. In no case has there been any appreciable growth of radium. The rate of production is certainly not greater than 1/10,000th part of that required by a direct change. Neither was any appreciable growth of actinium observed in a solution containing 278 grams of uranium, in 300 days, nor was there any appreciable growth of radium from Meyer and von Schweidler's feebly active residual deposit produced by long exposure of a charged wire to the actinium emanation. Levin,[73] examining uranium preparations of very different age since preparation, found in some cases a higher proportion of uranium in the freshly prepared than in the old specimens.

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[70] *Wien. Sitzungsber.*, 1907, **116**, IIA.

[71] *Ann. Report*, 1905, 308.

[72] *Abstr.*, 1907, ii, 730.

The subject has been carried a stage further by the researches of Rutherford [74] and Boltwood.[75] Both observed a steady increase in the amount of radium in actinium solutions with time. The former disproved the provisional conclusion of the latter,[76] that actinium was the direct parent of radium, by separating the radium-generating substance from actinium. He observed in his actinium preparations a steady growth of radium, in one case during 120 days, at the rate of $2{\cdot}5 \times 10^{-9}$ gram of radium per year. This rate of growth was unaffected by precipitating the actinium solution with ammonia, and redissolving the precipitate in acid, although this treatment removed almost all the radium ready formed. Removal of actinium X, also, did not affect the rate, showing that radium was not formed as the direct end-product of the actinium disintegration. In precipitation with ammonium sulphide a large part of the actinium remains in solution, and it was found that this fraction did not produce any radium. In concluding that the parent of radium is a substance distinct from actinium the reservation is made that it is too early to say whether there is any generic connexion between the two substances or not.

Boltwood's method of separating the parent of radium from uranium minerals consists in adding thorium nitrate to the solution and separating the thorium, which carries with it both actinium and the parent of radium, by means of several successive precipitations with oxalic acid. The rate of production of radium in this preparation was found to be constant during 500 days. He was unable to repeat Rutherford's separation by means of ammonium sulphide, but succeeded with sodium thiosulphate. He shows that the substance, so separated from actinium and capable of generating radium, possesses a characteristic α- and β-ray activity, which is proportional to its power of producing radium. In one preparation, consisting of 0·5 gram of thorium oxide, the activity was equal to 5 grams of uranium oxide, and no detectable amount of actinium was present. But for the small fraction due to thorium, the activity consists of α- and β-rays, both of a very low penetrating power. The α-rays are less penetrating even than those of polonium, and have a range less than 3 cm. of air. The β-rays are more easily absorbed than those of uranium. A quantitative separation of the new body from uraninite was attempted, and it was calculated that its activity is 0·8 of that due to the radium associated with it in the mineral. Allowing for the short range of the α-particle, this is quite consistent with the view that the body occupies an intermediate position in the uranium-radium series. Boltwood suggests the name "ionium" for the new substance, and considers it probable that it is a constituent of actinium preparations as usually prepared. It resembles thorium so closely in its chemical behaviour that it has not yet been separated from this element.

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[73] *Abstr.*, 1907, ii, 922.

[74] *Ibid.*, 1908, ii, 6.

[75] *Ibid.*, 1907, ii, 836.

[76] *Ann. Report*, 1906, 364.

O. Hahn[77] has confirmed these results. In the series of thorium preparations of known age since preparation (p. 325), he found that the greater the age of the preparation the more radium was contained therein. The minerals from which these substances are extracted contain, on the average, 5 per cent. of thorium and 0·3 per cent. of uranium. A growth of radium was observed, and its rate measured, in a new specimen of thorium nitrate initially free from radium. Precipitating the thorium as oxalate also precipitated the radium-producing substance. Measurements of the radium content of the thorium preparations of varying age up to six years gave indirectly the rate of growth of radium. The amount of radium associated with the thorium in the mineral can be calculated from the amount of uranium, and is the amount in equilibrium, both with the uranium and the intermediate parent. Assuming the latter and the thorium to be completely separated together in the manufacturing processes, the period of radium may be calculated from the rate of growth of radium in the thorium preparations, for the amount produced per year in this way must balance the amount of radium disintegrating per year. The period so found was between 3250 and 2630 years. This method of calculation involves the assumption that the new body is the direct parent of radium, and considering the nature of the calculation and the incompleteness of the data, the agreement is as near as can be expected. These experiments show that, had thorium preparations been examined for growth of radium on the same scale as uranium preparations were, the parent of radium would have been discovered several years ago.

[77] *Abstr.*, 1907, ii, 921.

The discovery is notable in that it constitutes the second instance, of which helium was the first, of the observed generation of an element, radium, the elementary character of which has been placed beyond doubt by ordinary chemical and spectroscopic methods.

Radium.

Mme. Curie[78] has redetermined the atomic weight of radium with 0·4 gram of pure radium chloride, a quantity more than four times greater than that used in the original determination. Purification by fractional crystallisation in dilute hydrochloric acid was carried out until the strongest line in the barium spark spectrum was only faint in comparison with a neighbouring line of medium intensity in the radium spectrum. An addition of 0·61 per cent. of barium chloride increased the intensity of this barium line so strongly that it was estimated that not more than 0·1 per cent. of barium could be present in the radium preparation used. Difficulties were at first encountered, owing to the radium being partly precipitated by minute traces of sulphuric acid, in the reagents, not capable of being detected by any other test. The reagents were therefore all specially prepared for the work. The chlorine in the anhydrous chloride, prepared by drying for half an hour at 150°, was estimated with silver as before, all the weighings being performed on a Curie aperiodic balance. The mean of three consecutive concordant experiments gave 226·2 ($Ag=107·8$, $Cl=35·4$) for the atomic weight, assuming the element to be bivalent. This is about a unit higher than the original determination, and may probably be accepted, in spite of the small quantity of material, with considerable confidence.

F. Rinne[79] has published a careful comparison of the crystallographic relation between the bromides of radium and barium, and has shown that radium bromide crystallises in the monoclinic system, and is isomorphous with, and crystallographically closely related to barium bromide.

Radium Emanation.

Kolowrat,[80] investigating the disengagement of emanation from radium-barium chloride and fluoride by heating, has found that at no temperature below the fusing point of the salt is all the emanation evolved, so that this method cannot be used instead of solution for extracting emanation for measurement. The salt was first fused to remove all emanation, and that regenerated in a definite time at a definite temperature, blown out, and measured. The amount of emanation disengaged in a definite interval is a function of the temperature. For the chloride, less than 1 per cent. of the amount formed escapes in the cold, and this is not increased by heating up to 350°. The fraction liberated then rises rapidly up to a temperature of 830°, when it is 90 per cent., but falls to 60 per cent. at 920°, and becomes 100 per cent. at 945°, the fusion point of the salt.

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[78] *Abstr.*, 1907, ii, 729.

[79] *Jahrb. Radioakt. Elek.*, 1906, **3**, 239.

[80] *Abstr.*, 1907, ii, 729.

Rümelin[81] has determined the period of radium emanation by a new method, suggested by Rutherford, in which a quantity of the emanation is sealed up in two connected glass tubes of widely different volumes. After keeping for two days in a room at constant temperature, the connexion between the tubes is sealed, and the tubes separated. The amount of emanation in the smaller tube is first determined in an electroscope, and some days later, when the amount in the larger tube has decayed to a value near that initially in the smaller tube, it also is determined in the same electroscope. Knowing the time that has elapsed between the measurements and the ratio of the two volumes, the decay period of the emanation, assuming it to be exponential, can be very accurately determined. The values for eight experiments all fell between 3·70 and 3·80 days, and the mean was 3·75 days. This is almost exactly the same as the original value (3·71 days) found by Rutherford and Soddy.

Sir William Ramsay has published during the year the results of numerous important investigations on the radium emanation, both of its physical characteristics and its chemical action on other substances, some of which are of a remarkable and unaccountable character. He verified[82] the observation of Rutherford and Barnes, of the heat evolved from the emanation, by enclosing the latter, derived from 162 milligrams of radium bromide, in a hollow bulb blown within the bulb of a thermometer. This showed at first a difference of 0·5° to 0·7° above the temperature of a similar comparison thermometer, but the difference diminished regularly from day to day, and at the end of twenty days became inappreciable. He next examined the decomposition of water by radium solutions, which, as is well known, invariably results in the production of an excess of hydrogen. In a series of six analyses there was a mean excess of hydrogen of 5·51 per cent. over the proportion required to form water. Emanation mixed with oxygen attacks mercury, but in hydrogen no action occurs. The various possible sources of the excess of hydrogen are discussed. The view that it is a product of radioactive change is improbable on account of its great quantity. No bromine or ozone is liberated, and bromate

[81] *Abstr.*, 1907, ii, 836.

[82] *Trans.*, 1907, **91**, 931.

or hydrogen peroxide could not be detected in an old radium bromide solution. Quantities of emanation were sealed up with water in exhausted glass bulbs, and shaken continuously for a month. In three experiments it was found that 1·81, 3·56, and 4·02 c.c. of gas were produced, containing respectively 2·91, 3·81, and 14·5 per cent. excess of hydrogen. Proof of the absence of hydrogen peroxide in the water was obtained by allowing the liquid to evaporate in a vacuum, and absorbing the vapour with phosphoric oxide. In a later experiment,[83] evidence of a small quantity of hydrogen peroxide was obtained by the use of ether and titanium sulphate. Emanation mixed with dry hydrogen and oxygen caused combination of the mixture to the extent of about 30 per cent., but not much change in the initial excess of hydrogen. Emanation separated from the excess of hydrogen, by explosion with the requisite quantity of oxygen, was introduced into several c.c. of water, and the rate of evolution of hydrogen and oxygen measured. The rate of generation of gas was found to fall off approximately exponentially with the time, with a period of about 2·53 days. In this experiment the gas was in contact with the tap of the burette, with the result that carbon dioxide was formed. The total volume generated was 2·14 c.c., which contained 0·85 c.c. of carbon dioxide and 0·47 c.c. of excess hydrogen after explosion.

Sir William Ramsay and A. T. Cameron[84] subjected a solution of copper sulphate to the action of the radium emanation, in the expectation that copper would be deposited, equivalent to the excess of hydrogen found in the experiments with water. No copper was deposited, but a trace of lithium and a considerable quantity of sodium were found in the copper solution. This experiment was repeated four times, and always, after separation of the copper, a residue weighing 1 to 2 milligrams was left, which showed the sodium lines strongly, and the lithium red line distinctly, in the flame spectrum. In one experiment the quantity of lithium was estimated at 0·00017 milligram. In a blank experiment, in which no emanation was introduced, the residue, after removing the copper, was less (0·79 milligram) than in the former case, and showed sodium, but no lithium, in the spectroscope. Pure water treated in a similar manner with emanation gave a residue of 0·71 milligram, showing sodium but no lithium.

In the fourth experiment with copper sulphate, the gas extracted at the end of the operation was found to consist largely of nitric oxide, together with carbon dioxide, hydrogen, oxygen, and some 10 per cent. of nitrogen. On sparking the nitrogen residue with oxygen over alkali, the residual gas showed the spectrum of pure argon, and no helium lines were visible. The gas from the experiment with emanation and water gave a residue showing a brilliant neon spectrum, in which the helium lines were faintly visible. A slight difference was also noticed in the copper that had been treated with emanation, in that the filtrate, after the precipitation of the copper as acetylide, gave a minute black precipitate with hydrogen sulphide, too small for further investigation, but not given in a blank experiment with untreated copper.

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[83] *Trans.*, 1907, **91**, 1604.

[84] *Ibid.*, 1593.

The authors attribute this truly remarkable series of results to the enormous energy evolved in the disintegration of the radium emanation, and suggest (1) that helium and the α-particle are not identical; (2) that helium results as the product by the degradation of the large molecule of emanation under bombardment by the α-particles; (3) that alone, or mixed with hydrogen or oxygen, the emanation is degraded into helium; (4) if heavier particles are present, for example, liquid water, the degradation of the emanation is less complete, and neon is produced; (5) in the case of the still heavier copper sulphate molecule, argon is the product. They also suggest that lithium, and possibly sodium, are products of the degradation of copper. These hypotheses are put forward tentatively. The results are described as preliminary, and are being repeated, as far as possible, without the use of glass, in order to avoid the possible introduction of sodium into the preparations.

Sir William Ramsay and A. T. Cameron [85] have also investigated the volume and the volume changes of the radium emanation, obtained from 87·7 milligrams of radium (element). This is a much larger quantity than was used in earlier investigations.[86]

In four experiments, the initial volume of the emanation, accumulating during the period of half-transformation of the emanation (3·88 days), was found to be between 0·337 and 0·182 cu. mm. compared with 0·222, the value originally found by Ramsay and Soddy. They give reasons for the conclusion that the larger of the two volumes is probably the more accurate, and take 1·162 cu. mm. for the volume of emanation formed per gram of radium per day. The curious phenomenon of the rapid initial diminution of volume was investigated in detail. Always, during the first hour and a half, the volume shrinks to one-half, according to an exponential law, and then remains relatively constant. Then a slow, continuous diminution ensues nearly at the same rate, for the first four days, as that at which the emanation suffers transformation. The initial change is ascribed to the association of monatomic to form diatomic molecules. The effect of raising the temperature was investigated. At 80°, 90 per cent. of the diatomic molecules, on the preceding hypothesis, suffer dissociation, but at 132° only 40 per cent. The initial association proceeds strictly exponentially with a period of 0·0764 (minute $^{-1}$). Taking the volume 1·162 cu. mm. as the amount of monatomic radium emanation formed per gram of radium per day, the value of the period of radium, on the assumption that one atom of radium produces one atom of emanation, is 236 years. This is many times less than the value first given by this method, and usually accepted from other evidence. It is necessarily a minimum value. The experiments were carried out with capillary tubes, both of glass and of quartz, and the absorption of various gases in the tubes determined. A dark, semi-metallic deposit was formed in the top of the tubes from the emanation, and this is believed to consist of radium *D*. The application of Boyle's law to the emanation was rigorously confirmed.

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[85] *Trans.*, 1907, **91**, 1266.

[86] *Ann. Report*, 1904, 273.

Active Deposit of Radium.

Mme. Curie[87] has investigated the cause of the concentration of the active deposit of radium at the bottom of closed vessels containing the emanation, noticed by P. Curie. The lower surface of a horizontal plate in the emanation becomes only one-half to one-fifth as active as the upper surface. The action is due to gravity, and is independent of the presence of dust, taking place even when the dust has been removed by expansion of the air over water. In dried air, and in a vacuum of 2 or 3 cm. mercury, the action is not produced. In other gases, also, the effect is found to be dependent upon the presence of water vapour.

The cause of the alteration of the rate of change of the active deposit of radium at high temperature[88] still remains unelucidated. Bronson[89] attributed the result to experimental errors, due to an unequal volatilisation and condensation of radium *C* in the sealed tube containing the emanation during heating. Radium bromide was heated in a sealed quartz tube, and its activity measured, while being heated, by means of the γ-rays. No change was noticed up to 1600°, when emanation began to escape from the tube. Makower and Russ[90] have measured the rate of decay of the emanation, kept throughout at 1100° in a sealed quartz tube, except during the actual periods of measurement, which was done with the tube cold. The rate of decay was the same as in the cold, but the activity was distinctly lower at the high temperature, and rose in the first few hours after cooling. Wires made active by exposure to the emanation were also tested, and here, again, heating in sealed glass or quartz tubes caused a somewhat irregular diminution of activity of between 3 and 15 per cent. for temperatures between 900° and 1200°. After the heating, the difference between the heated and unheated portion of the wires steadily diminished, due to the activity of the former decaying at a slower rate than the normal. Increasing the period of heating beyond five minutes exerted little influence, and the conclusion is drawn that the activity of radium *C* suffers some change at high temperature, in agreement with the statement of Curie and Danne, and contrary to that of Bronson.

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[87] *Abstr.*, 1907, ii, 728.

[88] *Ann. Report*, 1906, 347.

[89] *Abstr.*, 1907, ii, 216.

[90] *Ibid.*, 421.

W. Wilson and W. Makower[91] noticed that, when the ionisation due to the non-penetrating rays from the active deposit is exactly balanced against that produced by the penetrating rays of another part of the same active deposit, the balance alters as the activity decays, owing to the feebly penetrating β-rays of radium *B*, which decay at a rate different from the α-rays from radium *C*. The effect is small, and amounts to less than one per cent. of the total.

Radiolead and Lead.

Hofmann and Wölfl,[92] in separating radiolead from ordinary lead, found on distilling the chloride with ammonium chloride the active substance (radium *D*) is volatilised first. Much better results are stated to have been obtained by the use of Grignard's reaction. The dry chloride is subjected to the action of magnesium phenyl bromide in benzene, and part of the lead converted into lead tetraphenyl, which is found to be almost free from active matter.

St. Meyer and E. von Schweidler,[93] in their work on the electrolysis of the acetate solution of radiolead,[94] came to the conclusion that radium *E* consisted of two successive products, which they designated radium E_1 and radium E_2. With gradually increasing current strength, at first only radium *F* (polonium) is deposited, then radium E_1 and radium *F* together, and, lastly, all the four products. Radium E_1 is rayless with a period of 6·5 days, volatile at a red-heat, soluble in hot acetic acid, and electrochemically less noble than radium E_2. The latter has a period of 4·8 days, gives β-rays, is not volatile at 1000°, and stands electrochemically between radium E_1 and radium *F*. Thus is explained the conflicting results obtained by Rutherford and other workers on the period of this substance. If this explanation is correct, it is of interest to note that in radium *D* and radium E_1 we have two successive rayless changes, a sequence which, in most cases, would be difficult to unravel. By fractional crystallisation of the chloride from hot water, radium E_2 and radium F remain in solution, whilst radium D and radium E_1 separate out. (Compare J. Danysz, jun.[95])

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[91] *Phil. Mag.*, 1907, [vi], **14**, 404.

[92] *Abstr.*, 1907, ii, 521.

[93] *Wien. Sitzungsber.*, 1906, **115**, II*a*, 697.

[94] *Ann. Report*, 1906, 365.

In a later paper, the same authors[96] attempt to determine the period of radium D from simultaneous determinations of the initial α-activity (due to radium C) and initial β-activity (due to radium C), and, later, after the rapid changes are completed, the residual α-activity (due to radium F) and the residual β-activity (due to radium E_2) of a plate made active by exposure to the emanation of radium for 263·6 days. These four measurements suffice to determine, on certain assumptions, by mathematical analysis, the period of radium D when the other periods are known. Assuming equal ionising effects from each of the α- and β-particles respectively concerned in the activity, the ratio of the initial to final α-activity leads to a value for the period of radium D of about 19·5 years. Correcting for the known difference in ionising power between the α-particles of radium C and radium F, which stands in this respect in the ratio of 1 to 0·613, the period becomes twelve years. In the case of the β-rays, the uncorrected calculated period is 35·7 years, but the correction in this case is indefinite and cannot be applied. All that can be said is that it must increase the value of the period given. In attempting to explain this great discrepancy, they consider the shorter period the more trustworthy, and ascribe the value found from the evidence of the β-rays to the existence of two or more successive β-ray changes in radium C. Rutherford (p. 311) suggests that the change of radium C is double, on totally distinct evidence. Further indications that twelve years is about the true period of radium D, instead of Rutherford's value of forty years, found from the β-ray evidence, follows from the time taken for the residual α-ray activity of a plate exposed for a short time to the radium emanation to reach its maximum. This should be 949 days if the period of radium D is forty years, and 714 days if the period is twelve years. In two experiments it was found that the activity had already passed its maximum in two years.

Elster and Geitel[97] have concluded that the active constituent they separated from common metallic lead and its commercial salts[98] is radium F, for the value of its period of decay, the range of its radiation in air, the chemical method of its separation, and its property of depositing upon a copper plate, are all in favour of this view. It is derived from a trace of radium D present in common lead, and in agreement with this a specimen of lead 100 years old was found to be quite inactive. McLennan[99] found that the conductivity of air in lead cylinders, which is always much greater than in cylinders of other metals, varies widely with different samples of lead, and the lowest value was found for a specimen that had been in the laboratory from twenty-five to thirty years. There is therefore little doubt that the activity of lead is not an intrinsic property, but is due to radium products present in the ore, and separated during extraction.

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[95] *Abstr.*, 1906, ii, 644.

[96] *Ibid.*, 1907, ii, 664.

[97] *Ibid.*, 423, and *Physikal. Zeitsch.*, 1907, **8**, 776.

[98] *Ann. Report*, 1906, 365.

Potassium.

N. Campbell and A. Wood[1] state that potassium salts have an activity, specific and characteristic for the element, and proportional to the proportion of potassium in the salt. The rays consist entirely of the penetrating type. A sheet of paper, which cut down the activity of lead to one-half, exerted no effect on the rays from potassium salts. Measured in the usual way, the activity appeared to be about eight times greater than that of lead, but owing to the greater penetrating power of the potassium rays the activity is really greater than appears by this comparison. Compared by the β-rays, potassium showed about one-thousandth of the activity of uranium. No emanation was detected from the salts, and the activity was found to be the same for all commercial sources of potassium as for the potassium in wood ashes and in orthoclase. The rays are heterogeneous and of all degrees of penetrating power from that of the β-rays of uranium to much less. Rubidium salts possess an activity of the same order as the salts of potassium, but the rays are much less penetrating, and, allowing for absorption in the substance, the specific activity of rubidium must be twelve times that of potassium. Cæsium, lithium, and sodium salts are inactive. N. Campbell[2] subjected the rays from potassium to the action of an electric field, and obtained results which he considered proved conclusively that the rays are deviated like the β-rays of uranium, only, as an average, somewhat more readily. The sign of the charge carried could not be determined by the method employed, and it must be mentioned that the effects relied upon appear to have been extraordinarily minute. No other observations bearing on this subject have as yet appeared.

Natural Radioactivity.

H. W. Schmidt[3] measured the conductivity of the air, and the emanation content of the air and spring water, at various places in the mines at St. Joachimsthal, and found, as is to be expected, quite abnormal conditions. The emanation content of the spring water flowing directly from the uranium ore was found, for example, to be 120 times greater than that from the "Orange spring" at Kreuznach, yet, on account of the much greater volume of the latter, the actual amount of emanation brought to the surface was in each case much the same. Any articles left in the mine rapidly became radioactive, and the natural leak of the electroscope due to penetrating rays inside the mine was 100 to 400 times greater than outside. This leak was increased ten times when the air of the mine had access to the inside of the instrument. Many other papers dealing with the radioactivity of natural water have been published.[4]

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[99] *Abstr.*, 1907, ii, 731.

[1] *Ibid.*, 217.

[2] *Ibid.*, 597.

[3] *Physikal. Zeitsch.*, 1907, **8**, 1.

A. Battelli, A. Occhialini, and S. Chella[5] have examined the gas extracted from the water of the S. Giuliano spring, Tuscany, which contains a radioactive gas presenting peculiar features. About 100 c.c. of gas can be extracted from a litre of water, and consists of 84·65 per cent. of carbon dioxide, 3·12 per cent. of oxygen, and 12·22 per cent. of nitrogen. The activity of the gas decayed strictly exponentially after the first three days, but at a rate considerably slower than in the case of the radium emanation. The period is given as 8 days, 15 hours. The active deposit also decays at a slower rate than that from radium, the period being 54 minutes. Confirmation of these results must be awaited. Experiments are described in which the emanation was concentrated by removal of the carbon dioxide and condensation with liquid air, and sufficient of it was obtained to render a zinc sulphide screen bright enough to read a watch by.

A. S. Eve[6] has investigated the ionisation over the North Atlantic Ocean, which appears rather unexpectedly to be of the same order as over Europe and America. The amount of radium in sea-water is quite insufficient to account for this ionisation, and is only from 1/500 to 1/1000 of the average amount determined by Strutt in sedimentary and igneous rocks.[7] He has also determined[8] the amount of radium emanation in the atmosphere in the neighbourhood of Montreal, directly, by passing large volumes of air through charcoal at the ordinary temperature, and expelling the absorbed emanation by heat. The amounts varied in four experiments over a range of about 5 to 1, and the average amount per cubic metre of air is expressed as that furnished by 80×10^{-12} gram of radium. This is of correct order to account for the amount of radium *C* which may be collected on a negatively charged wire from the atmosphere, and, assuming 5 per cent. of the total amount of emanation escapes into the atmosphere from the ground, it is calculated that a depth of the earth's crust of one or two metres contains enough radium to supply the observed amount of emanation in the atmosphere to the height of 5 kilometres. This makes the results obtained for the ionisation over the ocean very surprising. Eve and D. McIntosh[9] examined the radium content of nine specimens of typical igneous and sedimentary rocks, found in the neighbourhood of Montreal, and found values agreeing closely with those given by Strutt for rocks from other parts of the world. It was found necessary to obtain the rocks in a state of fusion, as otherwise a varying and different proportion of emanation was expelled from different rocks. Addition of sulphuric acid to the solution of one of the rocks caused a diminution to one-fifth of the amount of emanation evolved.

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[4] A. Schmidt, *Abstr.*, 1907, ii, 218; F. Heinrich, *ibid.*, 150; F. Jentzsch, *ibid.*, 1908, ii, 9; F. B. Wade, *J. Amer. Chem. Soc.*, 1907, **29**, 941; G. Accola. *Nuovo Cim.*, 1907, **5**, 13, 444; C. Biella, *ibid.*, 526; Zambonini, *Abstr.*, 1907, ii, 663; G. Ercolini, *Ann. Soc. Chi., di Milano*, 1907, **13**, No. III–IV; E. Ebler, *Curtius, Festschrift*, 1907, 87; Engler and Sieveking, *Chem. Zeit.*, 1907, **31**, 811.

[5] *Physikal. Zeitsch.*, 1907, **8**, 65.

[6] *Phil. Mag.*, 1907, [vi]. **13**, 248.

[7] Compare F. B. Wade, *J. Amer. Chem. Soc.*, 1907, **29**, 941.

[8] *Abstr.*, 1908, ii, 7.

G. A. Blanc[10] finds the active deposit drawn from the atmosphere at Rome to consist very largely of the thorium active deposit. For several days' exposure of the charged wire, no less than 50 to 70 per cent. of the total activity was due to thorium. This is of interest in view of the extremely short period of the thorium emanation, and shows, what is well known in the laboratory, that the non-volatile products of the emanations persist and accumulate in the air, being probably deposited upon dust particles, and so remaining suspended for long periods. A. Wood and N. Campbell[11] have found a diurnal periodicity in the conductivity of air in closed vessels, which resembles closely the periodicity shown by the atmospheric potential, and N. Campbell[12] calls attention to an inexplicable sudden increase in conductivity on applying flame to an ionisation vessel. On withdrawing the flame, the ionisation again quickly becomes normal.

Various.

S. J. Allen[13] describes a null method of measuring ionisation by means of the quadrant electrometer, in which the ionisation to be measured is balanced against the saturation current in another chamber, produced from a surface coated with uranium oxide, which can be covered or exposed at will by means of a slide. The whole apparatus, together with the electrometer, is mounted as one in a convenient form.

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[9] *Abstr.*, 1907, ii, 729.

[10] *Phil. Mag.*, 1907, [vi], **13**, 378.

[11] *Ibid.*, 365.

[12] *Ibid.*, **14**, 614.

[13] *Ibid.*, 712.

Lancien,[14] having stated that uranium molybdate possessed an activity of forty uranium units, Szilard[15] repeated the work and found the activity completely normal, being proportional to the amount of uranium in the compound.

A. van der Broek[16] suggests a modified form of Prout's hypothesis, in which the α-particle, or half helium atom, is the unit out of which atoms are built up. There is room for 120 such hypothetical conglomerates, called alphads, up to the atomic weight of uranium, and these he arranges in fifteen series of periods containing eight elements. Although the individual atomic weights differ widely—up to 17 per cent.—from the corresponding weights of the alphads in the same position in the periodic table, the sum of the known atomic weights differs by only 0·06 per cent. from the sum of the weights of the corresponding alphads. Elements are therefore simply modified alphads.

Attempts have been made, so far without much success, to detect atomic changes in ordinary matter by thermal methods. C. B. Thwing[17] wound thermo-couples radially on a mica ring, so that the alternate junctions came on the outside and inside circumference of the ring, which was then placed between two cylinders of metal, in order to detect any difference of temperature between the inside and the outside of the cylinder. The whole was set up in a calorimeter, packed round with ice, and the thermo-currents read by a galvanometer. After twelve to twenty hours, perfectly steady deflections were obtained, corresponding, for example, with a temperature gradient of 0·000020° per cm. for lead, and 0·000103° for aluminium oxide. Serviss[18] repeated the above work with slight alterations and modifications in the method, and obtained completely negative results. Greinacher[19] has also examined the question. He determined by thermo-couples the temperatures of various salts, and found for many a temperature 0·01° above their surroundings, but lead nitrate showed the peculiarity of remaining from one to several hundredths of a degree lower than its surroundings. In no case was the heat generated greater than a few millionths of that generated by radium, and as a greater effect than this is scarcely to be expected, the experiments are not sufficiently delicate to be conclusive.

Some valuable summaries of the literature of special subjects

[14] *Abstr.*, 1907, ii, 697.
[15] *Ibid.*, 731.
[16] *Ibid.*, 523.
[17] *Phys. Review*, 1906, **23**, 315.
[18] *Amer. J. Sci.*, 1907, [iv], **24**, 452.
[19] *Abstr.*, 1907, ii, 836.

have appeared in the *Jahrbuch der Radioaktivität und Elektronik* during the year. H. W. Schmidt (iv, 195) writes on the first members of the radium disintegration series (radium A, B, and C); St. Meyer and E. von Schweidler (iii, 381) on the end members (radium D, E_1, E_2, and F); P. Ewers (iv, 78) on α-rays; Pohl (iv, 100) on the light emission produced in gases by radioactive substances; and J. Stěrba (iv, 306) on the chemical action of the cathode-rays. At the meeting of the Bunsen Society for Applied Physical Chemistry in Hamburg in May, 1907, a day was devoted to radioactivity, and the following papers were read and discussed (fully reproduced in the *Zeitsch. Elektrochem.*, 1907, **13**, 369 to 400): "Radioactivity" (Introductory), by Voller; "Chemical Behaviour of Radioactive Substances," by Marckwald; "Production of Helium from Radioactive Substances," by G. Meyer; "Nature of Radioactive Radiations," by F. von Lerch; "Theory of Atomic Disintegration," by Hahn; "Age of Minerals and Influence of Radium on the Heat of the Sun and Earth," by Levin; "Activity of Air and Springs," by F. Henrichs. A general discussion of great interest followed.

FREDERICK SODDY.

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